3 1761 06706021 0

Digitized by the Internet Archive
in 2007 with funding from
Microsoft Corporation

http://www.archive.org/details/absorptisolution00joneuoft

C
J774ab

THE ABSORPTION SPECTRA OF SOLUTIONS

OF

CERTAIN SALTS OF COBALT, NICKEL, COPPER, IRON, CHROMIUM, NEODYMIUM, PRASEODYMIUM, AND ERBIUM IN WATER, METHYL ALCOHOL, ETHYL ALCOHOL, AND ACETONE, AND IN MIXTURES OF WATER WITH THE OTHER SOLVENTS

BY

HARRY C. JONES AND JOHN A. ANDERSON

342605
1.4.30.

WASHINGTON, D. C.
PUBLISHED BY THE CARNEGIE INSTITUTION OF WASHINGTON
1909

CARNEGIE INSTITUTION OF WASHINGTON
Publication No. 110

PRESS OF J. B. LIPPINCOTT COMPANY
PHILADELPHIA

PREFACE.

This investigation, which is a continuation of the work of Jones and Uhler on the absorption spectra of solutions (Carnegie Publication No. 60), was carried out with the aid of a Grant generously awarded by the Carnegie Institution. Salts of the following metals were brought within its scope: Cobalt, nickel, copper, iron, chromium, neodymium, praseodymium, and erbium; and about 1,200 solutions were studied.

Spectrograms of salts of these metals in water, varying the concentration but keeping the total amount of coloring matter in the path of the beam of light constant, were obtained. In a similar manner spectrograms were made, keeping the total number of molecules in the path of the beam of light constant. The effect of such dehydrating agents as calcium chloride and aluminium chloride, on absorption in solution, was also studied.

A large number of salts were rendered anhydrous and dissolved in methyl alcohol, ethyl alcohol, and acetone. The concentration of the solutions in these solvents was varied, but the total amount of coloring matter in the path of the light was kept constant. Finally, water was added to the non-aqueous solutions, and its effect on absorption determined.

Perhaps the most striking result was obtained with anhydrous neodymium chloride in alcoholic solutions, to which small, increasing amounts of water were added. Here entirely new bands appeared on the addition of a small amount of water.

An ample supply of the salts of neodymium and praseodymium was furnished us with their characteristic liberality by the Welsbach Light Company, and our thanks are especially due to their chemist, Dr. H. S. Miner.

We accept this opportunity to extend our thanks to Prof. J. S. Ames, who has placed at our disposal the ideal conditions under which this investigation was carried out.

Harry C. Jones.

CONTENTS.

CHAPTER I.

PAGE

Introductory 1
  Apparatus 6
  Photographic Material, etc 7
  Sources of Light 8
  Making a Spectrogram 9

CHAPTER II.

Salts of Cobalt 11
  Cobalt Chloride in Water—Beer's Law 13
  Cobalt Chloride in Water—Number of Ions in the Path of the Beam of Light Constant 15
  Cobalt Chloride in Water—Molecules Constant 15
  Cobalt Chloride in Methyl Alcohol—Beer's Law 16
  Cobalt Chloride in Ethyl Alcohol—Beer's Law 17
  Cobalt Chloride in Acetone—Beer's Law 18
  Cobalt Chloride in Methyl Alcohol with Water 19
  Cobalt Chloride in Ethyl Alcohol with Water 20
  Cobalt Chloride in Acetone with Water 21
  Cobalt Bromide in Water—Beer's Law 22
  Cobalt Bromide in Water—Molecules Constant 22
  Cobalt Bromide with Calcium Bromide 23
  Cobalt Bromide in Methyl Alcohol—Beer's Law 25
  Cobalt Bromide in Ethyl Alcohol—Beer's Law 25
  Cobalt Bromide in Acetone—Beer's Law 26
  Cobalt Bromide in Methyl Alcohol with Water 27
  Cobalt Bromide in Ethyl Alcohol with Water 27
  Cobalt Bromide in Acetone with Water 28
  Cobalt Nitrate in Water—Beer's Law 29
  Cobalt Nitrate in Water—Molecules Constant 30
  Cobalt Sulphate in Water—Beer's Law 31
  Cobalt Sulphocyanate in Water—Beer's Law 32
  Cobalt Sulphocyanate in Water—Molecules Constant 33
  Cobalt Acetate in Water—Beer's Law 34
General Summary of Results with Cobalt Salts 35

CHAPTER III.

Salts of Nickel 39
  Nickel Chloride in Water—Beer's Law 39
  Nickel Chloride in Water—Ions Constant 40
  Nickel Chloride in Water—Molecules Constant 41
  Nickel Chloride in Water with Calcium and Aluminium Chlorides 41
  Nickel Sulphate in Water—Beer's Law 42
  Nickel Acetate in Water—Beer's Law 43

CHAPTER IV.

Salts of Copper 45
  Copper Chloride in Water—Beer's Law 45
  Copper Chloride in Water—Molecules Constant 46
  Copper Chloride in Methyl Alcohol—Beer's Law 46
  Copper Chloride in Ethyl Alcohol—Beer's Law 47
  Copper Chloride in Acetone—Beer's Law 48

CHAPTER IV. Salts of Copper.—Continued. PAGE

Copper Chloride in Methyl Alcohol with Water ... 49
Copper Chloride in Ethyl Alcohol with Water ... 50
Copper Chloride in Acetone with Water ... 50
Copper Bromide in Water—Beer's Law ... 51
Copper Bromide in Water—Molecules Constant ... 52
Copper Bromide in Methyl Alcohol—Beer's Law ... 52
Copper Bromide in Ethyl Alcohol—Beer's Law ... 53
Copper Bromide in Methyl Alcohol with Water ... 54
Copper Bromide in Ethyl Alcohol with Water ... 54
Copper Nitrate in Water—Beer's Law ... 55
Copper Nitrate in Water—Molecules Constant ... 56

CHAPTER V.

Salts of Iron ... 59
Ferric Chloride in Water—Beer's Law ... 59
Ferric Chloride in Water—Molecules Constant ... 59
Ferric Chloride with Calcium Chloride ... 60
Ferric Chloride with Aluminium Chloride ... 60
Ferric Chloride in Methyl Alcohol—Beer's Law ... 61
Ferric Chloride in Ethyl Alcohol—Beer's Law ... 61
Ferric Chloride in Acetone—Beer's Law ... 62

CHAPTER VI.

Salts of Chromium ... 63
Chromium Chloride in Water—Beer's Law ... 64
Chromium Chloride in Water—Molecules Constant ... 65
Chromium Chloride with Calcium Chloride and Aluminium Chloride ... 65
Chromium Nitrate in Water—Beer's Law ... 66
Chromium Nitrate in Water—Molecules Constant ... 67

CHAPTER VII.

Salts of Neodymium, Praseodymium, and Erbium ... 68
Preparation of Anhydrous Salts ... 71
Neodymium Chloride in Water—Beer's Law ... 72
Neodymium Chloride in Water—Molecules Constant ... 76
Neodymium Chloride in Water with Calcium Chloride and with Aluminium Chloride ... 77
Neodymium Chloride in Methyl Alcohol—Beer's Law ... 77
Neodymium Chloride in Ethyl Alcohol—Beer's Law ... 78
Neodymium Chloride in Mixtures of Methyl Alcohol and Water ... 79
Neodymium Chloride in Ethyl Alcohol with Water ... 83
Neodymium Chloride—Anhydrous ... 84
Neodymium Bromide in Water—Beer's Law ... 86
Neodymium Nitrate in Water—Beer's Law ... 87
Neodymium Nitrate in Water—Molecules Constant ... 91
Neodymium Nitrate in Methyl Alcohol—Beer's Law ... 91
Neodymium Nitrate in Ethyl Alcohol—Beer's Law ... 92
Neodymium Nitrate in Acetone—Beer's Law ... 92
Neodymium Nitrate in Mixtures of Methyl Alcohol and Water ... 93
Neodymium Nitrate in Mixtures of Acetone and Water ... 94
Praseodymium Chloride in Water—Beer's Law ... 94
Praseodymium Chloride in Mixtures of the Alcohols and Water ... 95
Praseodymium Nitrate in Water—Beer's Law ... 96
Erbium Chloride in Water—Beer's Law ... 97
Erbium Nitrate in Water—Beer's Law ... 97

CHAPTER VIII.

Summary and Conclusions ... 100

THE ABSORPTION SPECTRA OF SOLUTIONS.

BY

HARRY C. JONES AND JOHN A. ANDERSON.

CHAPTER I.

INTRODUCTORY.

The work on absorption spectra of solutions, of which this forms a part, was begun in the fall of 1905 and continued during the year 1905–6 by Jones and Uhler. The results obtained are given and discussed in "Hydrates in Aqueous Solutions," by H. C. Jones, Publication No. 60 of the Carnegie Institution of Washington. The first part of that work had to do with the effect of adding various dehydrating agents to solutions of colored salts; the second part dealt with the change in the absorption spectra produced by adding water to non-aqueous solutions. In the latter phase of the work, however, the concentration of the colored salt was varied in the solutions used in making any one spectrogram; but as the change in the spectrum observed was always the same qualitatively as would be expected from the change in concentration, it was deemed advisable to carry out again this part of the earlier work, keeping the concentration of the colored salt constant.

The salts used in the previous investigation were: Cobalt chloride, copper chloride, and copper bromide. In this investigation cobalt bromide was added to the above list of compounds. The resulting spectrograms show the same general change in the absorption as in the earlier work, thus proving that this was not due to change in concentration, but to some action of the water added.

If we assume that the absorption of light is due to vibrating, charged particles, or electrons, which are associated with ions, molecules, or groups of one or both of these, it is natural to expect that the character of the absorption will, in general, depend upon the nature of the system with which the vibrating, charged particle is associated. In what follows, the system made up of the charged particle and whatever it is associated with will be spoken of simply as the "*absorber.*"

The simplest case of an absorbing solution would be one containing only one kind of "*absorber,*" and we shall speak of it as a "simple" absorbing solution. Such a solution does not in all probability exist, but is perhaps closely approached in such cases as the very dilute solutions of the salts of permanganic acid studied by Ostwald and others. In such a solution the absorption of light of a given wave-length would be simply proportional to the number of absorbers in the path of the light (Beer's law); and if the absorbers are not changed by adding more of the solvent, it follows at once that if the product of concentration and thickness of layer of the solution is kept constant, the absorption will be unchanged. Also, if we have a solution containing several kinds of absorbers, each acting independently of the others, the same statement would be true;

in other words, the absorption spectrum of a mixture of simple solutions will be the sum of the absorption spectra of the constituents.

If the concentration is very great, the absorbers may be so close together that they cease to act independently of each other; hence, even if the solution is a simple absorbing one, Beer's law *may* cease to hold if the concentration is very great. In general, however, we may say that for simple absorbing solutions or mixtures of these, Beer's law will hold.

Actual solutions always differ more or less from the ideal simple solutions on account of the changes produced by dilution. These changes are due to **association, dissociation,** and **solvation.**

The molecules of the dissolved substance may combine with each other, forming more or less complex aggregates, each of which will, in general, have its own peculiar power of absorbing light. The composition of the aggregates will depend upon temperature and concentration, and hence, if a solution containing such aggregates is diluted, we should expect to find deviations from Beer's law even if the temperature is kept constant.

The molecules of a great number of substances when dissolved dissociate into two or more ions, the amount of dissociation depending upon the concentration. It is to be expected that the absorption of the ions into which a molecule dissociates will be different from that of the molecule itself, and, consequently, on diluting an electrolyte we should expect to find deviations from Beer's law, unless the solution is so dilute that it may be considered as completely dissociated.

We may also have various combinations of molecules, aggregates of molecules or ions, not only with each other, but also with the molecules of the solvent, the nature of which will depend both on temperature and concentration, and each of which may have a different power of absorbing light. If a simple, colored electrolyte like cobalt chloride, for example, is dissolved in water, we see at once what a complicated system the solution is; and it is not surprising that, in spite of the great amount of work which has already been done on this one salt alone, we are still far from able to give a satisfactory account of its absorption spectrum.

A satisfactory account of the absorption of any salt in solution requires a knowledge of the kinds of absorbers the salt forms, and the amount of each for any given set of conditions. Given this knowledge, it would be necessary to determine what would be the absorption spectrum if the solution contained only one kind of absorber. This could be done as follows: Suppose a salt in solution gives rise to the absorbers A, B, C, D, E, etc., the amount of each of which is supposed to be known under all conditions of temperature, pressure, concentration, etc. Vary the conditions in such a way that all of the absorbers except, say, A are kept constant, and note the change in the spectrum; this change is due to A alone, since by hypothesis no other is varied. Repeat, only keep all except B constant, and so on. By this process of elimination we should eventually arrive at a complete knowledge of the absorption due to each absorber, and could hence predict beforehand exactly what would be the absorption of any solution whatever of the salt in question. Unfortunately our knowledge of the parts formed when a salt is dissolved is still very vague. We have methods for measuring dissociation, so we may regard the number of ions and the number of undissociated molecules as known for different conditions.

Regarding aggregates and solvates, however, our knowledge is very general, indeed. Determinations of molecular weights give some idea concerning the existence or non-existence of aggregates, and the methods of Jones and others furnish similar ideas about solvates; but the knowledge gained thus far is not definite enough to enable us to perform experiments along the lines indicated above. A great deal can, however, be learned not only about absorption, but also about the nature of solutions, by the study of absorption spectra under conditions which are varied as much as possible.

The methods commonly employed are:

(1) To keep the concentration constant, varying the depth of the cell and photographing the spectra of successive depths one beneath the other, so that the complete spectrogram gives an idea of the intensity of absorption for the different regions of the spectrum, besides locating the absorption bands.

(2) To keep the depth of cell constant and varying the concentration. The results here should be identical with those obtained by keeping concentration constant and varying the depth of cell, provided the solution is of such a nature that Beer's law holds; in general, however, the two methods give quite different results, owing to the change in the nature of the absorbers produced by dilution.

Another method is that followed in the present work, namely, to vary both depth of layer and concentration in such a manner that the product of the two remains constant. If the nature of the absorbers is not changed by dilution, this method leaves the number of absorbers in the path of the beam of light constant, and hence the spectrum for successive solutions should be identical; or, what amounts to the same thing, the width of the absorption bands as shown by the spectrogram should remain constant throughout. Any deviation from Beer's law would at once be seen by the bands changing in width or position as the concentration is varied.

A modification of this method, also employed in the present work, is to vary the depth and concentration in such a manner that the total number of ions, or the total number of undissociated molecules in the path of the beam of light remains constant. This is easily done as follows: Let the concentration be denoted by c, the ratio of the number of dissociated molecules to the total number put into solution by x, the depth of solution used by d; the number of ions in a cubic centimeter of the solution is then proportional to cx, and the number of undissociated molecules to $c(1-x)$. To keep the number of ions in the path of the beam of light constant it is only necessary to keep the product cxd constant; and to keep the number of undissociated molecules constant the product $c(1-x)d$ must remain constant. If the successive depths of solution to be used have been fixed arbitrarily, the concentrations are determined in the following way: From tables giving the values of x for different values of c the products cx and $c(1-x)$ are calculated for all values of c. Two curves are then plotted, one between cx and c, the other between $c(1-x)$ and c. Letting c_1, x_1, and d_1 represent the values of c, x, and d for the greatest concentration to be used, the values for any other concentration being represented by the same letters without subscripts, we have, respectively,

$$c_1 x_1 d_1 = cxd \qquad c_1(1-x_1)d_1 = c(1-x)d$$

or,

$$cx = \frac{c_1 x_1 d_1}{d} \qquad c(1-x) = \frac{c_1(1-x_1)d}{d}$$

The terms on the right are both known, and hence the products cx and $c(1-x)$ for any chosen value of d are known; and from the two curves the corresponding values of c may be read off directly.

Since more is known about dissociation than about association or solvation, it is only natural to try to see whether the observed changes in absorption can be explained by dissociation alone. If dissociation does not suffice, then we must conclude that other factors come in. The present work is devoted largely to a study of the absorption spectra of a large number of salts from the standpoint of dissociation.

Let us consider for a moment the kind of evidence obtained by the methods outlined, and what conclusions may be drawn from them. Consider first the possibility that an absorption band does not change in width or position with concentration, when the product of depth of layer and concentration is kept constant. The simplest explanation is that the absorption of the molecule and of the ions into which it breaks down on dissociation is the same. An excellent example of this type is furnished by the ultra-violet band of nickel sulphate (see Plate 28); also by the more dilute solutions of neodymium and praseodymium chloride.

Let us now consider cases where we have deviations from Beer's law. Take first the possibility that an absorption band widens with dilution, when the product of concentration and depth of layer is kept constant. This would indicate either that the band is due to ions, or that the ions have stronger absorption in the region considered than the undissociated molecules. By making a series of exposures, keeping the number of ions in the path of the beam of light constant, we can decide between the two possible explanations. If the band now remains of constant width and position, it is most likely due to ions alone; if it narrows on dilution, the ions have stronger absorbing power than the undissociated molecules; while if the band should widen with decrease in concentration, dissociation would in no way suffice to explain it.

The other case is where the band narrows with dilution, when the product of concentration and depth of layer is kept constant. If dissociation can account for this we must either have the undissociated molecules absorbing more strongly than the ions formed from them, or else the ions not absorbing at all. In the former case the band should widen with dilution when "undissociated molecules" in the path of the light are kept constant, while in the latter case the band would remain constant in width and position under the same conditions. If the band narrows with decrease in concentration when the number of undissociated molecules is kept constant, dissociation alone can not possibly explain the facts. An example of this case is furnished by the ultra-violet absorption of most copper salts in aqueous solution.

The case often met with in the present work where a band narrows with dilution when the product of concentration and depth of layer is kept constant, but widens when the number of undissociated molecules is kept constant, deserves further consideration, as dissociation may or may not be able to account for it, depending on the nature of the change in the band. This was discussed by E. Müller, who showed that by measurement of the extinction coefficient at various concentrations, using a spectrophotometer, we may determine whether Beer's law holds for each one of the three absorbers in a solution of an electrolyte, even when these have quite different powers of absorption. Work on this point is now in progress for the solutions showing the effect just spoken of, and the results will be published shortly.

Another interesting method of studying absorption spectra is to keep both concentration and depth of layer constant, and to vary the temperature. Much work of this kind has already been done by Hartley and others, and some work is now in progress in this laboratory. As is well known, changing the temperature has only a small effect on the dissociation, hence we may say that when the temperature is varied the dissociation remains roughly constant. The spectrum of some solutions, however, undergoes very great changes; for example, solutions of cobalt chloride which are red at room temperatures become blue when the temperature is elevated sufficiently; and according to Donnan and Bassett solutions of the same salt in ethyl alcohol, which at ordinary temperatures are blue, turn red when cooled down to —75° C. This effect, which involves the appearance or disappearance of a complicated set of absorption bands in the red, can evidently not be accounted for by dissociation, since it takes place when the dissociation is known to change but very slightly.

In the present work considerable attention has been given to solutions in non-aqueous solvents, such as methyl alcohol, ethyl alcohol, and acetone, as well as to solutions in mixtures of these solvents with water. In this part of the work great care has been taken to have both the salts and solvents as free from water as possible, and this is of fundamental importance, as is shown by the spectrograms of solutions of neodymium chloride in mixtures of alcohol and water, where it appears that the change in the spectrum produced by 1 per cent or less of water may easily be detected.

The question of the effect of the solvent comes up in this connection, and this in turn involves the more general question as to the condition of a molecule of a dissolved substance in any solvent whatsoever. Does it form some kind of a compound with the solvent, or does it move about freely in the solvent without materially changing its nature? Kundt's law, which states that the effect of the solvent upon absorption is simply to shift the position of the absorption bands, these being located nearer the region of long wave-lengths the greater the dispersion of the solvent, seems to imply that the molecule of the dissolved substance exists in the free state in solutions. If this view be taken, then the effect of the solvent should not be very great, especially if solutions in solvents having similar optical properties are compared. If, on the other hand, a salt when it goes into solution always forms some sort of a compound with the solvent, we might expect to find radical differences in the absorption.

It is evident that a study of the absorption spectra of a salt when dissolved in various solvents ought to bring out many points of interest as bearing upon the question of the nature of solutions.

APPARATUS.

For visual examination of solutions a small, direct-vision, grating, pocket spectroscope was always at hand, and was found very useful for the purpose of examining solutions in order to determine what particular range of concentrations it was desirable to work with. Judging from the color of the solution as seen by the unaided eye was found to be very unsatisfactory, since many solutions have very wide absorption bands which may give the solution quite a decided tint, even when the absorption is so feeble that it would be almost impossible to obtain a satisfactory photographic record of it. On the other hand, when solutions have narrow, intense absorption bands, like the salts of the rare earth metals, the solution may show practically no color to the unaided eye, and still the absorption bands may be quite intense as seen in the spectroscope.

For photographing the spectra, the vertical grating spectrograph used by Jones and Uhler was employed. In its original form as used by them films 2.5 by 7 inches were employed, on which the spectrum from λ 2000 to λ 6300 could be registered.

In the present work it was decided to remodel it so as to allow the whole spectrum from λ 2000 to λ 7600 to be photographed, and accordingly the camera and the camera end of the box were enlarged so as to hold films 2.5 by 9 inches. Owing to the fact that the grating has only 10,000 lines to the inch, it was not possible to add the extra 2 inches to the red end of the camera, which, if it could have been done, would have left the grating-axis very near the middle of the spectrum; the 2 inches being actually added to the ultra-violet end, which necessitated turning the grating-axis farther away from the slit, thus placing it in a point of the spectrum some little distance beyond the visible violet. The spectrum is, however, near enough to normal, even at the extreme red end, to make any correction unnecessary, unless measurements of a very high degree of accuracy are required.

For holding the aqueous solutions, the cell illustrated in figure 66, page 172, of "Hydrates in Aqueous Solution," was employed throughout, while for non-aqueous solvents the cell shown by Plate 22 of the same work was used.

PHOTOGRAPHIC MATERIAL, ETC.

It was at first decided to use films coated with the panchromatic emulsion made by Wratten and Wainwright, of Croyden, England, as this emulsion has been found to be very uniformly sensitive to light of all wave-lengths between λ 2000 and about λ 7400. The makers, however, did not succeed in producing a satisfactory film in time for the present work, and hence it was necessary to use the Seed L-Ortho-film for the region from λ 2000 to about λ 6000, and to make a separate exposure for the red end of the spectrum, using for this purpose Wratten and Wainwright panchromatic glass plates, cut to such lengths (4 to 4.5 inches) that the curvature of the focal plane would not introduce any appreciable difficulty. This method very nearly doubled the time and work consumed in making the spectrograms, as two separate sets of exposures had to be made with each set of solutions. It also made it very difficult to get the two negatives of such intensities that they would match satisfactorily, owing not only to the different absolute sensibility of the two emulsions to light of a given wave-length, but also to the different rates at which the photographic blackening increases with time for the two emulsions.

Plate 1 gives some idea of the sensibility of the photographic plates used to light of different wave-lengths, and also shows how the photographic action increases with time of exposure. A is a series of exposures of the Wratten plate to the spectrum of the Nernst filament, the times of exposure being 2, 4, 6, 8, 15, and 30 seconds, and 1 and 2 minutes, respectively. 0.8 ampere of alternating current flowed through the filament and the slit was adjusted to a width of 0.01 cm. The strip on the negative corresponding to the 2-seconds exposure shows some photographic action from λ 3800 to λ 7250 with faint maxima near λ 4700, λ 5400, λ 5950, λ 6500, and λ 6950, respectively; the corresponding minima falling near λ 5050, λ 5600, λ 6100, and λ 6700. The minimum at λ 5050 is much more pronounced than any of the others, but it is interesting to note that even at the middle of this one there is considerable photographic blackening produced by the 2-seconds exposure. The maxima and minima show most distinctly in the two strips corresponding to 6-seconds and 8-seconds exposure, respectively; which shows that at first the photographic action in the maxima increases with time somewhat more rapidly than in the minima. The λ 5050 minimum is still visible in the 1-minute exposure, while the others can be seen only with difficulty. In a full exposure (1 to 2 minutes) the photographic action in the red begins to shade off perceptibly at λ 7250, but is still considerable as far as λ 7500. B is a series of exposures of the Seed L-Ortho-film; the successive times of exposure being 2, 3, 4, 8, 15, and 30 seconds, and 1 minute, respectively. The current in the filament, width of slit, and development were exactly the same as used in making the negative for A. The strip corresponding to the 2-seconds exposure shows maxima at λ 4700 and λ 5600, and a minimum at λ 5250, at the center of which the negative records *no photographic* action whatever. The maximum at λ 4700 in the 2-seconds exposure is slightly stronger than the one at λ 5600, while the reverse is the case in the strips corresponding to exposure of 4 seconds or more. The action increases with time much more rapidly with yellow light than with blue light. The action in the minimum also increases more rapidly with time than is the case with the λ 5050 minimum of the Wratten plate. With a full exposure (1 minute) blackening of the Seed film begins to shade off at λ 5900, but may be seen as far as λ 6200.

The developer used throughout was a concentrated hydrochinone solution made up according to Jewell's formula (Astrophys. Journ., 1900, pp. 240–243).

SOURCES OF LIGHT.

The most satisfactory source for the region of the spectrum lying between the extreme red and the beginning of the ultra-violet is the Nernst lamp, as it is brilliant enough to bring the time exposure down to about a minute, and is, of course, perfectly continuous and steady. In the ultra-violet the spectrogram on Plate 1 shows that its action decreases rapidly with the wave-length, ceasing practically at about λ 3200. For this region, then, some spark-spectrum must be used. The cadmium zinc spark used by Jones and Uhler is fairly satisfactory, being especially strong in the extreme ultra-violet, but it has the disadvantage of having a limited number of very intense lines on a rather faint, continuous background. It was hoped that some spark-spectrum could be found having a very large number of lines, but without any lines of very great intensity.

A reference to published tables of the spectra of the elements showed that tungsten, molybdenum, and uranium all satisfied this requirement. Each of these has so many lines, and these so closely packed, that with an instrument of moderate dispersion the spectrum ought to be nearly continuous. The problem was to make spark terminals of these substances which could be used satisfactorily. The metals not being easily obtainable, the following plan was tried: Sheet carbon about 3 mm. thick was cut into pieces about 1 cm. by 4 cm. and dipped into concentrated solutions of ammonium molybdate, or uranium nitrate; a suitable solution of a tungstate was not tried. These pieces of carbon were then heated to redness in a Bunsen flame and again quickly immersed in the solution, the process being repeated two or three times. Some pieces were also treated with solutions of salts of iron, copper, and cobalt, and others were treated with two or more of the solutions in succession. The spectra of these carbon terminals showed the lines of the metals with which they were treated almost as well as terminals of the metals themselves; but in the case of iron, copper, or cobalt the cyanogen bands were also present. With molybdenum and uranium, however, the cyanogen bands were absent, the merest trace of the λ 3883 band appearing. The uranium spectrum is almost continuous with the dispersion employed, but its intensity falls off very rapidly from λ 3000 towards the ultra-violet. The molybdenum spectrum, although not so nearly continuous, is much richer in ultra-violet, being quite strong as far as λ 2300.

Curiously enough, if a pair of carbon terminals is treated with molybdenum and also with one or more of the other metals, very little except the molybdenum spectrum is seen. Uranium, however, seems to increase the intensity of the continuous background somewhat, and hence the terminals finally used were prepared by dipping twice in the molybdate solution and then three times in the solution of uranium nitrate.

It was also found that the terminals charged with various metals wore away at quite different rates when the spark was passed. Those dipped into a solution of a copper salt wore away at the rate of a millimeter or more per minute, while those treated with molybdenum could be used for hours without appreciable wear. The character of the spectrum given by these molybdenum-uranium terminals may be seen from any of the plates reproduced in the following chapters, which do not show complete absorption in the ultra-violet.

The coil used to produce the spark was a large Röntgen X-ray coil, through the primary of which was passed an alternating current of from 5 to 8 amperes, 60 cycles; and across the secondary terminals was shunted a capacity of about 0.011 microfarad. The spark used was about a centimeter in length, and was placed about 15 cm. above the slit, the direction in which the spark passed being perpendicular to the length of the slit. By this arrangement the grating received light from all parts of the spark at the same time. In order to produce a uniform photographic strip of the proper width, it was necessary to keep the spark terminals moving in a direction parallel to the length of the slit, which was done by hand; a suitable stand being used. Care was taken to move the spark-holder always at the same rate, namely, a to-and-fro motion was executed in about 4 seconds, which insured equality in times of exposure for the different strips of the spectrograms. The intensity of the spark undoubtedly varied somewhat, due to fluctuations of the voltage impressed upon the primary terminals of the coil; but this was found to be so small that no provision was made for regulating it. The Nernst filament is, however, so sensitive to slight changes in voltage that a variable resistance was placed in series with it; by regulating which the current was always kept at 0.8 ampere during an exposure.

MAKING A SPECTROGRAM.

In making a spectrogram consisting of seven photographic strips with a comparison spectrum, the following was the usual sequence of operations: Seven separate solutions were made up, the quantity of each being usually 25 c.c. The cell to be used, having been cleaned and dried, was filled to the required depth with the most concentrated solution of the series, and the quartz plates limiting the depth of the solution adjusted to parallelism. The exposure to the Nernst lamp was then made, the current being kept at 0.8 ampere by hand regulation of the variable resistance in series with it. The usual time of this exposure was 1 minute. An opaque screen covering up the visible spectrum as far down as λ 4000 was then interposed between the grating and the photographic film, and the exposure to the light of the spark in the ultra-violet was made. The duration of this exposure was usually 2 minutes. The photographic film was then moved a distance of 6.5 mm. into the proper position for the next exposure. The cell was emptied and rinsed out with a few drops of the next solution, and the series of operations repeated for the second strip, and so on. It was always found advisable to clean the slit-jaws after each exposure, and also to see that the image of the Nernst filament fell in the proper position on the slit.

After the film had been exposed and the comparison spark spectrum impressed, it was necessary to make a series of exposures on a panchromatic plate for the red end of the spectrum, using the same set of solutions. No exposure to the spark was made in this set except for the narrow comparison strip. As the extreme red end of the plate was at about λ 7600, λ 3800 of the second order would overlap the first order here. Accordingly an absorbing screen was always used in making the exposures for the red end of the spectrum. This screen consisted of two glass plates separated by a layer of Canada balsam a little less than a millimeter thick. It absorbed all radiations of shorter wave-length than λ 3900.

The scale accompanying the spectrograms in the following chapters was made by photographing an ordinary paper scale. Several photographs were made, the distance between the paper scale and the lens of the camera being varied slightly from exposure to exposure. The resulting negative which fitted the majority of the spectrograms best was selected and used throughout. Absolute accuracy is not to be expected, owing to the fact that both photographic films and the paper on which prints from these were made, contract more or less in drying, and different films or papers contract differently. λ 5000 on the scale was always placed in coincidence with the corresponding wave-length on the photographic strips; the correction for the ends of the spectrograms differs slightly for the different plates, but never amounts to more than about 25 or 30 Ångström units.

CHAPTER II.

SALTS OF COBALT.

Jones and Uhler,[1] in their work on the absorption spectra of salts of cobalt and copper, discussed a number of the more important papers dealing with cobalt, so that it is necessary only to make brief reference to them here.

Babo [2] observed a number of the color changes produced in cobalt salts by change in temperature, or by addition of a dehydrating agent. Similar observations were made by Gladstone [3] and Schiff.[4]

Bersch[5] proposed the view that there are two modifications of the compound $CoCl_2.6H_2O$—the one red and the other blue—and would thus account for the color changes in cobalt salts with rise in temperature.

Tichborne [6] would also account for these color changes on the basis of hydration, and Vogel's [7] work pointed in the same direction.

The investigations of Russell[8] on the absorption spectra of solutions of cobalt salts are important. He worked under various conditions, such as with the fused salt, with its solution in concentrated hydrochloric acid, and with solutions in the various alcohols and glycerol. He also studied the effect of changes in temperature on the absorption spectra. He concluded, as the result of all of his work, that the color of the aqueous solutions was due to the presence of hydrates.

Potilitzin [9] showed that the conclusion of Bersch, that there are two modifications of the compound $CoCl_2.6H_2O$, is an error, and that the formation of blue cobalt chloride from the red modification is always a dehydration phenomenon.

Etard [10] studied the color changes and also the solubility curve of cobalt chloride and iodide, and showed from the sudden changes in the direction of the solubility curves the existence of various hydrates of these salts. He also studied the changes in the absorption spectra of cobalt chloride with changes in temperature.

Engel [11] does not believe that any general theory can be advanced to account for the changes in color of cobalt salts, but thinks that the blue color is often due to the formation of double compounds. The blue color of a hot, saturated solution of cobalt chloride he regards as due to a double compound between the salt and the hydrochloric acid liberated as the result of hydrolysis.

---

[1] Publication No. 60, Carnegie Institution of Washington.

[2] Jahresber., 1857, 72.

[3] Journ. Chem. Soc., **10**, 79 (1859).

[4] Lieb. Ann., **110**, 203 (1859).

[5] Sitzungsber. Wien Akad., II, **56**, 726 (1867).

[6] Chem. News, **25**, 133 (1872).

[7] Ber. d. deutsch. chem. Gesell., **8**, 1533 (1875); **11**, 913 (1878); **12**, 2313 (1879).

[8] Proc. Roy. Soc., **32**, 258 (1881). Chem. News, **59**, 93 (1889).

[9] Ber. d. deutsch. chem. Gesell., **17**, 276 (1884), and Bull. Soc. Chim. (3), **6**, 264 (1891).

[10] Compt. rend., **120**, 1057 (1895); **131**, 699 (1900).

[11] Bull. Soc. Chim. (3), **6**, 239 (1891).

Wyrouboff[1] and Le Chatelier[2] show that Engel's view is untenable.

W. N. Hartley,[3] in his elaborate investigations on absorption spectra, has included a number of salts of cobalt. His experimental work consisted in observing and photographing the spectra of a large number of solutions of chlorides, bromides, iodides, nitrates, etc., of a fairly large number of metals, including cobalt. Some of the more interesting and important conclusions at which he arrived are the following, stated nearly in his own words.

When a definite crystalline hydrate is dissolved in a non-aqueous solvent, upon which it does not act chemically, the molecules of the salt remain unchanged in chemical composition.

In a series of anhydrous salts which do not form definite crystalline hydrates, the effect of rise in temperature up to 100° C. does not produce any alteration in their absorption spectra, other than that which results with substances which undergo no chemical change with such rise in temperature. The change in question is usually an increase in the intensity of the absorption, or a slight widening of the absorption bands.

Crystallized hydrated salts dissolved in a minimum amount of water at 20° C. undergo dissociation by rise in temperature. The extent of the dissociation may proceed as far as complete dehydration of the compounds, so that more or less of the anhydrous salt may be formed in the solution.

The most stable compound that can exist in a saturated solution at 16° C. or 20° C. is not always of the same composition as the molecule of the crystallized solid at the same temperature, since the solid may undergo a partial dissociation from its water of crystallization when the molecule enters into solution. When a saturated solution of a colored salt undergoes a great change in color or any remarkable change in its absorption spectrum upon dilution, the dilution is always accompanied by marked heat evolution.

Hartley[4] at the close of his paper on "The Absorption Spectra of Metallic Nitrates" has the following significant paragraph.

> The ultimate conclusion drawn from this work is that the operations of dissolving a salt and diluting the solution do not cause a separation of the compound into ions, but only a dissociation of such a character that the molecule is shown to consist of two parts, the movements of the one being influenced by those of the other, so that the molecule of the salt is, in fact, not completely resolved into ions, but is in a condition of molecular tension. The application of external energy, such as light or electricity, may, however, readily cause a separation such as may be brought about by electrolysis or by static electricity, and in some instances, by photographic action.

Ostwald[5] thinks that the red color of solutions of salts of cobalt is due to the cobalt ions.

---

[1] Bull. Soc. Chim. (3) **6**, 3 (1891).

[2] Ibid. (3), **6**, 84 (1891).

[3] Dublin Trans. (2), **7**, 253–312 (1900), and Journ. Chem. Soc., **81**, 571 (1902); **83**, 221 (1903).

[4] Journ. Chem. Soc., **83**, 245 (1903).

[5] Grundlinien d. anorg. Chem., 620.

The paper by Donnan and Bassett[1] should be especially mentioned in connection with the changes in color of cobalt salts. After citing a number of well-known facts, and adding a fairly large number of interesting new ones, they came to the conclusion that the blue color of solutions of cobalt salts is due to the formation of complex anions containing cobalt. Some of the evidence which they furnish merits very careful consideration in this connection.

Hartley[2] takes issue with the conclusions reached by Donnan and Bassett, interpreting the facts cited or discovered by them in terms of hydration and dehydration.

Cobalt Chloride in Water—Beer's Law. (See Plate 2 A and B.)

In both A and B, the strip corresponding to the most concentrated solution is adjacent to the numbered scale. The concentrations of the solutions used in making set A were 2.5, 1.88, 1.25, 0.83, 0.58, 0.42, and 0.31, respectively; the corresponding depths of cell were 3, 4, 6, 9, 13, 18, and 24 mm. The concentrations used in making set B were 0.83, 0.63, 0.42, 0.276, 0.192, 0.139, and 0.104; the depths of cell were the same as in set A. The exposures to the red end of the spectrum were omitted in this case, inasmuch as observations with the direct-vision spectroscope showed that the solutions, at least in such thicknesses of layer as were employed, were perfectly transparent from the beginning of the orange to the end of the red. The most concentrated solution in layers of 2 cm. or more showed faint traces of bands in the orange and red, but in layers of a few millimeters thickness these were of course quite invisible.

The spectrogram shows three regions of absorption: One in the green, middle near λ 5200; one in the ultra-violet, with its middle near λ 3300; and one in the extreme ultra-violet. The strips corresponding to the four most concentrated solutions of set A show only one absorption band in the ultra-violet, but the strip corresponding to the fifth solution shows transmission between λ 2800 and λ 3000, and absorption from λ 3000 to λ 3500; thus making it very evident that there are two regions of absorption. The strips corresponding to the three most concentrated solutions of set B also show very plainly the existence of the band at λ 3300, although the absorption is not complete even at the middle of the band. In the fourth strip of B, corresponding to a concentration of 0.276 and depth of cell equal to 9 mm., practically all trace of the band has disappeared, the spark spectrum appearing to shade off uniformly from λ 3600 to λ 2650, where it ends.

It will be noticed that the intensity of the spark spectrum in the region λ 2900 is greater for the strips near the numbered scale than for the fourth, fifth, and sixth strips. This is due partly to a gradual decrease in the intensity of the spark itself, while the spectrogram was made, produced by a gradual fall in potential of the source of alternating current operating the coil. That the effect is real, however, is shown by Plate 3 B, where a similar decrease in transmission at λ 2900 with dilution is recorded, and where the intensity of the spark was constant or very nearly so throughout. The increased intensity of the seventh strip of Plate 2 B is due to the fact that before making the exposure the potential was readjusted to its original value.

---

[1] Journ. Chem. Soc., 81, 939 (1902).

[2] Ibid., 83, 401 (1903).

The absorption in the extreme ultra-violet decreases regularly with dilution, the strip corresponding to the most concentrated solution in set B transmitting as far as λ 2650, while that corresponding to the most dilute solution shows transmission a little below λ 2500.

In set A the band in the green narrows quite rapidly at first, then more slowly with dilution. In set B it remains very nearly constant, especially in the strips corresponding to the more dilute solutions.

The facts brought out by the spectrogram may be summed up briefly as follows: When the product of concentration and depth of absorbing layer is kept constant, the absorption band in the green remains constant, except in very concentrated solutions, where it narrows somewhat with dilution; the one-sided, extreme, ultra-violet absorption decreases with dilution, while the band having its center near λ 3300 narrows very rapidly with dilution, disappearing entirely when a concentration of about quarter-normal is used in a layer about 1 cm. in depth. In the region λ 2800 to λ 3000 there is remarkable transparency in solutions having a concentration about half-normal. This transparency decreases somewhat with dilution to about one-tenth normal.

A comparison between this plate and Plate 2 in the work of Jones and Uhler already referred to, reveals a remarkable difference in the ultra-violet. The four strips nearest the comparison spectrum of their plate correspond to concentrations of more than 2.0 normal, and with a depth of absorbing layer of 0.67 cm., and yet the absorption in the region λ 3000 to λ 3500 is not very great. It might at first sight seem probable that the absorption band in this region was produced by some impurity in the cobalt chloride used. But this is improbable, since the salt from which were obtained the solutions used by Jones and Uhler and those used in the present work came from the same sample of material. Besides, Plate 23, in "Hydrates in Aqueous Solution," shows that the solution of the cobalt chloride used by Jones and Uhler, when dissolved in methyl alcohol, exerts strong absorption in the ultra-violet, while Plate 7 of the present work indicates only faint absorption in this region, the concentrations, depth of cell, etc., used in the two cases, not differing materially; hence, it is evident that it is not a question of the presence of an impurity. The probable explanation is that the discrepancy is due to a difference of temperature.

It is well known that the absorption of cobalt salts in solution is greatly affected by even slight changes in temperature, and if the λ 3300 band is especially sensitive, such variations of temperature as occur in the laboratory on different days might be sufficient to account for the changes in the spectrum observed. No data are at hand, however, giving the change of absorption in the ultra-violet produced by change of temperature, and hence this point will have to remain unsettled until the work now in progress shall have supplied the data for the absorption band in question.

Cobalt Chloride in Water—Number of Ions in the Path of the Beam of Light Constant. (See Plate 39 B.)

The concentrations were 2.00, 0.99, 0.546, 0.318, 0.205, 0.140, and 0.103, the corresponding depths of absorbing layer being 3, 4, 6, 9, 13, 18, and 24 mm., respectively.

Very little need be said about this spectrogram, since it shows that the absorption decreases rapidly with dilution, as was to be expected from the result when the product of concentration and depth of absorbing layer was kept constant. This spectrogram also shows the existence of the band at λ 3300, as well as indications of the decrease of transparency at λ 2900 with dilution from half-normal to tenth-normal. That an increase in absorption in this region is indicated in this spectrogram is significant, inasmuch as it shows that dissociation is not able to account for it. For the reason stated in the description of Plate 2, no exposure was made to the red end of the spectrum for this set of solutions.

Cobalt Chloride in Water—Molecules Constant. (See Plate 3.)

In both sets the strip corresponding to the most concentrated solution is adjacent to the numbered scale. The solutions were made up of such concentrations that the number of undissociated molecules of cobalt chloride in the path of the light should be constant for each set. The concentrations for set A were 2.50, 2.04, 1.53, 1.14, 0.885, 0.695, and 0.570; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm., respectively. The concentrations for set B were 0.70, 0.575, 0.434, 0.329, 0.253, 0.197, 0.158. The data used in calculating the concentrations were taken from the table on page 81 of "Hydrates in Aqueous Solution."

In making the exposures for set A only the light from the Nernst lamp was used, as a preliminary test showed that none of the solutions transmitted any light of shorter wave-length than λ 3850. Owing to the general absorption of concentrated solutions of cobalt chloride, it was necessary to increase the time of exposure, and hence for set A the light from the Nernst lamp was allowed to act for a period of 3 minutes through each of the solutions.

The exposures for set B were 1½ and 3 minutes, respectively, for the Nernst lamp and the spark. No exposures were made to the red end of the spectrum, since all the solutions showed uniform transmission to beyond λ 7600.

A shows that the band having its center at λ 3300 narrows with dilution, even when the number of molecules in the path of the beam of light is kept constant; thus demonstrating that the change in this band can not be accounted for by dissociation. The limits of transmission as given by the negative for the seven solutions beginning with the most concentrated are λ 4130, λ 4070, λ 3970, λ 3930, λ 3900, λ 3870, λ 3850, which shows that the band narrows more rapidly at first. In B this band may be seen in the three strips nearest to the numbered scale, corresponding to concentrations 0.70, 0.575, and 0.434, but it has practically disappeared in the fourth strip, corresponding to concentration 0.329. The maximum of transmission near λ 2900 is very well shown in B. The absorption in the extreme ultra-violet seems to remain sensibly constant in B, the limit of transmission being λ 2700 throughout.

The band in the green is peculiar. In A its violet edge moves farther down into the violet, and in such a way that the limits of transmission for the seven strips lie almost exactly on a straight line, the total displacement being 100 Ångström units or from λ 4550 to λ 4450. The red edge of the band at first moves towards the violet, then turns and moves towards the red as the dilution increases. On the whole the absorption band widens with dilution, but from concentration 2.5 to 1.14 its center moves towards the violet by about 50 A. U., after which it remains practically unchanged in position. In B the band widens with dilution and very nearly uniformly, the apparent asymmetry being due to the greater sensitiveness of the Seed film to yellow light.

Cobalt Chloride in Methyl Alcohol—Beer's Law. (See Plate 4.)

The concentrations of the solutions used in making the negative for A were 0.25, 0.21, 0.174, 0.143, 0.118, 0.100, and 0.083; the corresponding depths of cell were 8, 9.5, 11.5, 14, 17, 20, and 24 mm., respectively. For B the concentrations were 0.143, 0.120, 0.100, 0.082, 0.0675, 0.0572, and 0.0476; the depths of cell were the same as for set A. The most concentrated solutions had a very deep purple color which, as dilution increased, changed to pink. The solutions for set A exerted considerable general absorption, so that in order to get a satisfactory spectrogram the slit was opened to 0.015 cm. and the exposures to the Nernst lamp and spark were, respectively, 3 and 4½ minutes. In making the negative for set B the slit was set at 0.01 cm. and the exposures were 1½ and 3 minutes, respectively, for the Nernst lamp and spark.

Both A and B show a region of absorption in the extreme ultra-violet which narrows slightly with dilution. In A the limits of transmission for the most concentrated and most dilute solutions are λ 2630 and λ 2600, respectively, while in B the limit is at λ 2570 throughout. The strips corresponding to the more concentrated solutions (those nearest the numbered scale) in A show the presence of two faint absorption bands, having centers at λ 3100 and λ 3600, respectively. Both of these disappear gradually with dilution.

The absorption band in the green has its center at λ 5250 in both A and B. It narrows somewhat with dilution in A, whereas in B it remains of sensibly constant width.

In the orange and red is a rather complicated group of absorption bands, the absorption of the most concentrated solution of set A beginning at about λ 5850 and extending to a little beyond λ 7000. With dilution this absorption decreases rapidly, breaking up into bands, the position and character of which are as follows:

1. Fairly narrow band, with center at λ 5910; appearing on the negative as far as the sixth strip in A.
2. Band with center at λ 6050, which is visible in the strip corresponding to the fifth solution of A. This band and the one at λ 5910 are not clearly separated in the strips corresponding to the first and second solutions.

3. Fairly narrow, intense band, with center at λ 6240, which may be seen as far as the strip corresponding to the seventh solution.

4. Faint, rather wide band, with center at approximately λ 6450, and disappearing practically in the strip corresponding to the fourth solution. This band is nowhere clearly separated from the larger one at λ 6700.

5. Intense, wide band, with center at λ 6700, which narrows rapidly with dilution, but may be seen quite plainly in the negative strip corresponding to the most dilute solution of set A. It is also clearly visible in the strips corresponding to the three most concentrated solutions of set B, while the other bands are seen only with difficulty on this negative.

The transmission from λ 7000 to the end of the visible red is complete for all the solutions referred to on page 245 of "Hydrates in Aqueous Solution." In describing the absorption of cobalt chloride in methyl alcohol, Jones and Uhler say with reference to their observations on the absorption in the red: "If the solution could have been made more concentrated, or better, if the cell had been deeper, it is extremely probable that all the bands observed in aqueous solutions could have been seen with the alcoholic solution in question."

The above description of the bands shown on Plate 4, in conjunction with Jones and Uhler's curves on page 197, and their description of the absorption of cobalt chloride in water given on page 189, will show how very different the absorption spectra in question are. Not only are the locations of the centers of the bands very different, but the character of the group is so changed that it is difficult to see how it can be regarded as the same set of bands. Furthermore, Jones and Uhler's description on page 189, and their curves on page 197, show that the absorption in the concentrated cobalt chloride solution is quite different from that observed when a large amount of calcium chloride is added to a dilute solution of the salt. In the first case the three absorption bands noted had their centers at λ 7140, λ 6760, and λ 6360, whereas the curves for the second case show that these figures correspond to regions of maximum transmission. It might be argued that this indicates a shift of the position of the bands with addition of calcium chloride, but this is answered by Jones and Uhler, who find that with the addition of more of this salt the bands simply increase in intensity without change of position. The shift may, however, be due to a change in the concentration of the cobalt salt, but this point has yet to be investigated.

Cobalt Chloride in Ethyl Alcohol—Beer's Law. (See Plate 5.)

The concentrations of the solutions used in making the negative for A were 0.15, 0.126, 0.104, 0.086, 0.071, 0.060, and 0.050; the corresponding depths of cell were 8, 9.5, 11.5, 14, 17, 20, and 24 mm., respectively. For B the concentrations were 0.060, 0.050, 0.042, 0.034, 0.028, 0.024, and 0.020; the corresponding depths of cell being the same as used in making set A.

The color of the solutions as seen in the bottles was deep blue for the most concentrated, changing to a light greenish-blue in the most dilute. The general absorption observed in the concentrated solutions in methyl alcohol was quite absent in ethyl alcohol, so that in making the negatives for both A and B the slit was adjusted to a width of 0.01 cm. and the exposures to the Nernst lamp and spark were 1½ and 3 minutes, respectively.

The spectrogram shows a region of absorption in the extreme ultra-violet, which narrows regularly with dilution; the limits of transmission for the strips corresponding to the most concentrated and most dilute solutions of set A being, respectively, λ 2670, and λ 2630, while for set B they are λ 2580 and λ 2550.

The negative for set A also shows two absorption bands in the ultra-violet, having their centers roughly at λ 3100 and λ 3600. These bands are undoubtedly identical with those already noted in the same region for the solutions in methyl alcohol. One difference, however, is to be pointed out. The bands in the ethyl alcohol solutions are somewhat more intense, in spite of the fact that the concentration of the colored salt is smaller, and they also disappear much more slowly with dilution.

The absorption in the green is very much fainter in ethyl alcohol than in methyl alcohol; and measurement of the position of the center of the band indicates that it is located a trifle nearer the red in the former case. The position of the center was found to be at λ 5280. The band remains constant in width and position with dilution; A shows a region of intense absorption in the yellow, orange, and red, which narrows somewhat with decrease in concentration; the limits of transmission for the most concentrated solution being λ 5500 and λ 7170, and for the most dilute λ 5500 and λ 7060.

In B the absorption in this region of the spectrum is less intense, especially for the more dilute solutions, which show faint transmission throughout the band. The red edge of the band for the most concentrated solution is at λ 6970, while for the most dilute solution it is at λ 6800, the wave-lengths given corresponding to the limits of transmission as indicated by the photographic blackening of the negative. The strips corresponding to the more dilute solutions of set B show faint traces of bands, which appear to correspond roughly in position to the bands noted in the description of Plate 4. The bands at λ 5910 and λ 6050 only show faintly, and they both appear much less clearly defined than in the methyl alcohol solutions.

COBALT CHLORIDE IN ACETONE—BEER'S LAW. (See Plate 6.)

The concentrations of the solutions used in the negative for A were 0.0154, 0.0129, 0.0107, 0.0088, 0.0073, 0.0060, and 0.0051; the corresponding depths of cell were 8, 9.5, 11.5, 14, 17, 20, and 24 mm., respectively. For set B the concentrations were 0.0073, 0.0061, 0.0051, 0.0042, 0.0034, 0.0029, and 0.0024; the depths of cell were the same as in A. The solutions were all blue, the color merely changing from a dark to a rather light blue with dilution.

The spectrogram shows two regions of absorption, one in the ultra-violet and one in the red. The faint absorption indicated in the green is due to the diminished sensibility of the Seed film in this region.

The absorption in the ultra-violet is due entirely to the solvent, which may be inferred from the fact that it is the same in A and B, and also from the fact that it increases with dilution. This, of course, is due to the increased depth of the layer of the solvent. The limit of transmission for the 8-mm. layer falls at λ 3260, and for the 24-mm. layer at about λ 3320.

The absorption in the red is seen to be unchanged by dilution, or, as it may be stated, it obeys perfectly Beer's law. In A it consists of a band extending from λ 5500 to λ 7100, with faint transmission near λ 6000; thus indicating a band of absorption at λ 5700. B shows three wide and poorly-defined absorption bands, having their centers at λ 5725, λ 6200, and λ 6780, respectively. Of these, the last is much more intense than any of the others. No breaking up of these bands into narrower ones, as observed in solutions in the alcohols, can be noticed, although the transmission throughout the region of absorption in B is sufficient to allow the narrower bands to be seen if they existed. We must conclude, therefore, that the absorption spectrum of the acetone solution differs considerably from that of the alcohol solutions, which resemble each other very closely.

Cobalt Chloride in Methyl Alcohol with Water. (See Plate 7.)

In preparing the solutions used in making the negatives for this plate a fixed amount of the mother-solution of cobalt chloride in methyl alcohol was run into a measuring-flask, then the required amount of water added, and finally the flask was filled up to the mark with pure methyl alcohol. The concentration of the colored salt, therefore, remained constant throughout. Fourteen solutions were made up, the spectra of eight of which were photographed on one film and the remaining six on the other. Therefore, the line of separation of the two films falls between the eighth and ninth strips, counting from the numbered scale.

The concentration of cobalt chloride throughout was 0.088. The percentages by volume of water added were 0, 0.5, 0.75, 1, 1.25, 1.5, 2, 3, 3.5, 4, 5, 6, 8, and 10, respectively. The strip corresponding to the solution in pure methyl alcohol is adjacent to the numbered scale; the strip corresponding to the solution containing 10 per cent of water was at the top of the plate. The depth of cell was 2 cm., and the exposures to the Nernst lamp and spark were 1⅙ and 3 minutes, respectively; the slit was 0.01 cm. wide.

Two regions of absorption may be seen, one in the extreme ultra-violet and one in the green. The two absorption bands in the ultra-violet at λ 3100 and λ 3600, already described for Plate 4, were too faint to be recorded with certainty, and the merest trace of the absorption in the red is seen in the negative strip nearest the numbered scale. The band in the extreme ultra-violet narrows regularly with addition of water, the limits of transmission for the solution in pure alcohol and for the one containing 10 per cent of water being, respectively, λ 2650 and λ 2480.

The green band narrows markedly with increase of water. Its center also shifts slightly towards the blue, being at λ 5250 for the solution in pure methyl alcohol, and at λ 5210 for the solution containing the largest percentage of water.

The marked difference between the ultra-violet spectrum shown by this plate and that shown by Plate 23 in "Hydrates in Aqueous Solution" has already been mentioned. It is evident from the negatives that the solutions exert considerable absorption in the ultra-violet region, as the spectrum is faint compared with the comparison spectrum. If this absorption increases with rise of temperature, as is very probable, the difference noted might well be produced by a difference in temperature of only a very few degrees.

COBALT CHLORIDE IN ETHYL ALCOHOL WITH WATER. (See Plate 8.)

The concentration of cobalt chloride throughout was 0.088. The percentages of water, beginning with the solution used in making the strip nearest the comparison spectrum, were 0, 1, 2, 3, 4, 5, 5.5, 6, 6.5, 7, 7.5, 8, 9, 10, 11, and 12. The duration of the exposures to the Nernst lamp and the spark was, respectively, $1\frac{1}{6}$ and 3 minutes; the slit was adjusted to a width of 0.01 cm. The common depth of absorbing layer was 2.0 cm.

The four solutions containing the least amounts of water show the bands at λ 3100 and λ 3600 to be very intense, making the absorption for the solution in pure ethyl alcohol complete from λ 3800 to the end of the ultra-violet. The bands, however, disappear rapidly on addition of water, so that in the strip corresponding to 6 per cent of water they can hardly be noticed. This strip transmits light as far out as λ 2600, while on the strip made with the solution containing 12 per cent of water transmission extends to λ 2475.

The band in the green behaves very much the same as it does in methyl alcohol, being, however, somewhat fainter in ethyl than in methyl alcohol. Its middle for the solution containing 12 per cent of water is at λ 5200. For the solution in pure ethyl alcohol it is not possible to determine its middle, as it unites with the strong absorption band in the orange and red, this solution showing complete absorption from about λ 4930 to λ 7200.

The absorption band in the red narrows very rapidly with addition of water. Its limits for the solution containing 3 per cent of water are λ 5750 and λ 7000. In the strips which correspond to the solutions containing from 5 to 7.5 per cent of water, the band breaks up into a rather complicated spectrum. Absorption bands may be noticed having centers at λ 5910, λ 6060, λ 6240, λ 6400, and λ 6700. Of these, the last is the strongest and widest. The one at λ 6400 is very faint, the one at λ 5910 a little more intense; while those at λ 6060 and λ 6240 are fairly intense, comparing favorably with the bands in the same region seen on Plate 4.

Referring to the description of the negatives from which Plate 5 was made, it will be recalled that, although the absorption in the red showed signs of breaking up into finer bands, these did not appear very distinctly. Indeed, the only ones that could be made out were those at λ 5910 and λ 6060. The water added to solutions of cobalt chloride in ethyl alcohol must hence play an important part in the developments of these bands, and it is barely possible that the faint development of the bands noted in Plate 5 may have been due to slight traces of water which it is impossible to remove from the ethyl alcohol, or which might have found its way into the alcohol in the process of pouring the solution into the cell and exposing this in the spectrograph. It is probable that the activity of water in producing changes in the absorption spectrum depends not upon the percentage relation of water to alcohol, but of water to amount of salt in a given volume of the solution. This was found to be so for solutions of neodymium salts in mixed solvents, which will be discussed in the chapter dealing with the rare earths. In the event of this rule also applying to cobalt salts, we may say that since 5 per cent of water produces a fair development of the bands in a solution of concentration 0.088, it would require only about 1 per cent of water to do so for the most dilute solution used in making the negative for Plate 5, where the concentration was 0.02. The bands then were much less clearly developed, which in the event of their being caused by water would indicate the presence of water to an amount of say 0.5 per cent, which is well within the range of probability.

It is not at all improbable that the absorption bands in the red region of the spectrum, shown by solutions of cobalt salts dissolved in ethyl alcohol, could be used as a delicate test for the presence of water in the solvent.

Cobalt Chloride in Acetone with Water. (See Plate 9.)

The concentration of the cobalt salt throughout was 0.0108. The successive percentages of water were, beginning with the solution corresponding to the strip nearest the numbered scale, 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, and 30.

The solutions containing from 0 to 10 per cent of water were deep-blue to light-blue, while those containing from 16 to 30 per cent of water showed very little color except a faint suggestion of pink. The duration of the exposure to the Nernst lamp lasted 1 minute, that to the spark 3 minutes, with a slit width of 0.01 cm. The cell was adjusted to a depth of 3.0 cm.

The intense absorption in the ultra-violet is due to the acetone, and hence no transmission is noticed beyond λ 3300. The solutions containing the least amount of water show a region of absorption near λ 3600, which may be the same band that has already been described in discussing solutions in the alcohols. The solutions containing from 0 to 14 per cent of water show absorption in the orange and red, which decreases rapidly with increase of the amount of water.

The solution in pure acetone absorbs everything from λ 5400 to λ 7300. Both edges of the band approach each other rapidly until the solution containing 10 per cent of water is reached, when it breaks up into a number of narrower bands, their centers being at λ 5910, λ 6060, λ 6240, and λ 6700. The band at λ 6400, in the ethyl alcohol solution on addition of water, does not appear distinctly enough to be seen with certainty. In general, the system of bands is the same as that which is seen in ethyl alcohol, and is most likely due to the presence of water; since it will be recalled, from the description of Plate 6, that the solution in pure acetone shows no system of bands at all comparable with those here described. The proportion of water to salt in the solution, in order to show the bands, is very much larger for solutions in acetone than for solutions in ethyl alcohol, the values being about as 15 to 1.

The change in the spectrum produced by adding more water than 14 per cent is too slight to be noticed.

COBALT BROMIDE IN WATER—BEER'S LAW. (See Plate 10.)

The concentrations of the solutions used in making the negative for A were 2.14, 1.60, 1.07, 0.71, 0.49, 0.36, and 0.27, the corresponding depths of cell being 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.71, 0.53, 0.35, 0.24, 0.164, 0.12, and 0.09; the depths of cell were the same as in A. The strip corresponding to the most concentrated solution is in each case adjacent to the numbered scale.

The exposures to the Nernst lamp lasted 1½ minutes, while those to the spark lasted 3 minutes, the slit having a width of 0.01 cm.

The most concentrated solution had a deep reddish-brown color. With dilution the color gradually changed to the usual pink. No exposures were made to the red end of the spectrum, since even the most concentrated solution in layers of 2 cm. or more failed to show any absorption in this region.

The spectrogram shows two regions of absorption, one in the extreme ultra-violet and the usual one in the green.

The most concentrated solution of set A transmits the ultra-violet light of the spark as far as λ 2720, while the most dilute solution transmits as far as λ 2570. The absorption decreases with dilution much more rapidly at first, as is shown by the rounded appearance of the edge. The most concentrated solution of B transmits λ 2470, while the most dilute one lets through some light of wave-length λ 2350, being, therefore, almost perfectly transparent to all wave-lengths emitted by the spark used. No trace of an absorption band near λ 3300, such as was observed in aqueous solutions of cobalt chloride, could be noticed in the aqueous solutions of the bromide. In fact, the bromide is much more generally transparent to light of all wave-lengths than the chloride, and especially so for the ultra-violet region of the spectrum. The band in the green behaves very much like that due to cobalt chloride. It narrows rapidly at first with dilution, then more slowly, and finally remains of practically constant width in the four most dilute solutions of set B. The middle of the band in B is very near λ 5200, which is the same as in the case of cobalt chloride. The band is, however, considerably narrower in the bromide than in the chloride solutions, due in part to the slightly smaller concentration; but as this is hardly sufficient to account for the whole effect it indicates an intrinsic difference in the behavior of the two salts.

COBALT BROMIDE IN WATER—MOLECULES CONSTANT. (See Plate 11.)

No data giving the dissociation of cobalt bromide were at hand, and, accordingly, since it is a general rule that the chlorides and bromides do not differ greatly in this respect, the dissociation of the bromide was assumed to be the same as for cobalt chloride. Now it is possible that the actual value of the dissociation for any given concentration of the bromide might differ somewhat from the corresponding value for the chloride, and still the rate of change of dissociation with concentration might be sensibly the same for the two salts. And, evidently, in the calculation of the series of concentrations required in order to make the number of molecules in the path of the beam of light constant, for an arbitrary set of cell-depths, we are concerned only with the rate of change of dissociation with concentration, and not with the actual value of the dissociation for any given concentration. A comparison of the series of concentrations fulfilling the condition of "molecules constant" for various strong electrolytes used in the present investigation shows that they differ from each other by amounts that are small compared with experimental errors in the measurements of dissociation. Hence, the assumption made in the present case would not introduce any sensible error.

The concentrations used in making the negative for A were 1.53, 1.14, 0.885, 0.695, and 0.570; the corresponding depths of absorbing layer of solution were 6, 9, 13, 18, and 24 mm., respectively. For B the concentrations were 0.70, 0.575, 0.434, 0.329, 0.253, 0.197, and 0.158; the corresponding depths of cell were 3, 4, 6, 9, 13, 18, and 24 mm. It will be noticed that the concentrations for B, as well as the depths of cell, are identical with those used in making the negative for Plate 3, and, hence, a comparison of the two sets of spectra shows at a glance the relative absorbing power of cobalt bromide and cobalt chloride solutions. The latter exerts a considerably greater absorbing power throughout the spectrum.

The exposure to the Nernst filament and spark for both A and B lasted respectively 1¼ and 3 minutes, the width of slit being 0.01 cm. as usual. The spectrogram shows that the absorption in the extreme ultra-violet remains constant, the limit of transmission in A being at λ 2700, in B at λ 2470. The band in the green widens with dilution throughout, and quite uniformly, differing in this respect from the chloride, where it will be recalled that the band at first remained of constant width, and then began to widen with dilution. No exposure to the red end of the spectrum was made at all; the solutions transmitting freely light of all wave-lengths between λ 5700 and λ 7600.

COBALT BROMIDE WITH CALCIUM BROMIDE. (See Plate 12.)

The concentration of cobalt bromide throughout was constant and equal to 0.260. The concentrations of calcium bromide, beginning with the solution corresponding to the strip adjacent to the numbered scale, were 3.73, 3.56, 3.39, 3.22, 3.05, 2.88, 2.72, 2.54, 2.37, 2.20, 1.87, 1.53, 1.19, 0.85, 0.51, 0.00. The differences in concentration were, accordingly, 0.17, 0.17, 0.17, 0.17, 0.17, 0.17, 0.17, 0.17, 0.17, 0.34, 0.34, 0.34, 0.34, 0.34, 0.51.

The solution containing the greatest amount of calcium bromide was purplish-blue in color, from which the color changed to the reddish-pink of cobalt bromide in the solution containing no calcium salt.

The cell was adjusted to a depth of 1.1 cm. for each of the solutions; the exposures to the Nernst lamp and spark being, respectively, 1½ and 3 minutes. The solution containing no calcium bromide transmits all wave-lengths from λ 2400 to λ 7600, with the exception of the region λ 5000 to λ 5300 which is absorbed. With addition of calcium bromide the band in the extreme ultra-violet widens rapidly, so that in the solution pertaining to the tenth strip, counting from the scale, all radiations of shorter wave-length than λ 2800 are absorbed. In addition an absorption band having its center at λ 3010 makes its appearance, and increases rapidly in intensity and width with the increase in the amount of calcium bromide. In the solution corresponding to the eleventh strip, this band and the band in the extreme ultra-violet have run together, causing all light of wave-length shorter than λ 3140 to be absorbed.

The question whether all the absorption in the ultra-violet is due to the presence of calcium bromide as such, or whether it is due to some action of this salt on the cobalt bromide in the solution may be answered by referring to Plate 11 A, in "Hydrates in Aqueous Solution," and to the description of it given on page 208, as well as to Plate 10, which shows the effect on the absorption of cobalt chloride produced by adding calcium bromide of various concentrations. A concentrated solution of calcium bromide 4.236 normal, in a depth of layer of 1.41 cm., still transmits some light of wave-length shorter than λ 2800, although it exerts some absorption as far as λ 3100. Plate 10, "Hydrates in Aqueous Solution," shows that a solution of cobalt chloride containing calcium bromide in such concentrations as 0.7 normal, still transmits light of a wave-length as short as λ 2500 when the layer is 1.41 cm. deep, without any sign of absorption in the region λ 3010. We may accordingly conclude that the widening of the extreme ultra-violet band in Plate 12 is due to the absorbing action of calcium bromide, but that the band at λ 3010 is to be ascribed to the joint action of this salt and cobalt bromide.

The band in the green widens regularly and symmetrically with the addition of calcium bromide. Measurements on the negatives give the following results: For the strip pertaining to the solution containing no dehydrating agent, the limits of transmission are λ 5020 and λ 5300, center at λ 5160. For the strip corresponding to the solution containing the greatest amount of calcium bromide the limits were λ 4770 and λ 5560, center at λ 5165.

In the red the solutions containing the greatest amount of the dehydrating agent show a set of four absorption bands having their centers at λ 6400, λ 6650, λ 6950; the center of the fourth band lies in the extreme red, beyond the region of sensibility of the photographic plate used. Its presence is shown by the cutting off of the extreme red end of the strips nearest the numbered scale. The band at λ 6400 is rather narrow, the others moderately wide, the one at λ 6650 being the most intense and also persisting the longest with decrease in the amount of the calcium salt. A comparison of this spectrum with the diagram shown on page 197 of "Hydrates in Aqueous Solution," which shows the position and relative intensity of the red bands of cobalt chloride brought out by adding large quantities of calcium chloride, reveals some notable differences. The positions of the bands are sensibly the same, but in calcium chloride the band at λ 6950 is stronger than the one at λ 6650, whereas the reverse is true for the bromide. Also, the chloride shows a weak band at λ 6400 with stronger ones at λ 6240, and λ 6095, while the bromide has an intense band at λ 6400, and none at all in the other positions. The bands with the chloride were the same whether calcium chloride, calcium bromide, or aluminium chloride was used as a dehydrating agent, thus indicating that the difference in the spectra which we have just considered is to be referred to the colored salt and not to the dehydrating agent.

COBALT BROMIDE IN METHYL ALCOHOL—BEER'S LAW. (See Plate 13.)

The concentrations of the solutions used in making the negative for B were 0.228, 0.191, 0.158, 0.130, 0.108, 0.091, and 0.076; the corresponding depths of absorbing layer were 8, 9.5, 11.5, 14, 17, 20, and 24 mm. For set A the concentrations were 0.114, 0.096, 0.079, 0.065, 0.054, 0.045, and 0.038. The depths of absorbing layer were the same as for set B. The concentrations were accordingly about 9 per cent smaller for B than was the case in the similar set for cobalt chloride, and about 18 per cent smaller in case of A.

The most concentrated solution was slightly purplish in color, from which the color changed to the usual pink of cobalt solutions. The concentrated solutions had very little general absorption, differing in this respect markedly from those of cobalt chloride in the same solvent. The exposures to the Nernst lamp and spark were, respectively, 1¼ and 3 minutes, the slit being, as usual, 0.01 cm. in width.

The edge of the ultra-violet band is perfectly straight in both sets, showing that Beer's law holds rigidly. The limit of transmission in B is λ 2850, while for A it is λ 2760, thus indicating much stronger absorption in this region for the bromide than for the chloride. The chloride, although transmitting some light of shorter wave-length, does, however, exert a greater amount of absorbing action in the region below λ 3700, since it has two bands, one at λ 3100 and one at λ 3600, both of which are entirely absent in the bromide solution. The band in the green is not as intense as in the chloride solution. Its center is at λ 5250, and it narrows slightly with dilution in both B and A.

The slight absorption in the red, which was undoubtedly present in the most concentrated solution, was not sufficient to be registered on the photographic plate. This, accordingly, indicates complete transparency from the green band to beyond λ 7400.

COBALT BROMIDE IN ETHYL ALCOHOL—BEER'S LAW. (See Plate 14.)

The concentrations of the solutions used in making the negative for A were 0.146, 0.122, 0.102, 0.084, 0.069, 0.058, and 0.044, the depths of cell being 8, 9.5, 11.5, 14, 17, 20, and 24 mm. The concentrations for B were 0.058, 0.049, 0.040, 0.033, 0.026, 0.023, and 0.019; the depths of cell were the same as for A. The concentrations were accordingly almost the same throughout as those used in making the negative for Plate 5, so that the two are directly comparable.

All the solutions were blue, the color becoming very faint, however, in the most dilute solutions of set B. Exposures and slit-width were the same as for Plate 13.

There is strong absorption in the extreme ultra-violet which, however, narrows slightly with dilution; the limits of transmission being λ 3060 and λ 3000 for the most concentrated and most dilute solutions of

A, respectively, and λ 2920 and λ 2820 for those in B. No trace of any bands at λ 3100 or λ 3600, as found in the corresponding solutions of cobalt chloride, can be seen. The green band may be seen in A, but unlike the chloride solution there is a region of complete transparency on the red side of it. In B the green band is so extremely weak that the slight shading noticeable near λ 5250 may be due to the lack of sensibility of the Seed film in this region.

In A there is a wide region of complete absorption, which narrows rapidly with dilution, breaking up into two absorption bands in B. The limits of transmission for the most concentrated solutions of A are λ 5750 and λ 7200, while for the most dilute solutions the figures are λ 6150 and λ 6900. It appears, therefore, that the red edge of the absorption band is a little nearer the region of long wave-lengths than is the case for the corresponding solutions of cobalt chloride.

B shows two absorption bands having their centers at λ 6160 and λ 6730, respectively. Both narrow rapidly with dilution, disappearing practically in the most dilute solution. No trace of the narrower bands seen in the chloride solution is visible.

Cobalt Bromide in Acetone—Beer's Law. (See Plate 15.)

The concentrations of the solutions used in making the negative for A varied from 0.037 to 0.012; the depths of absorbing layer were 8, 9.5, 11.5, 14, 17, 20, and 24 mm. In B the concentrations were varied from 0.012 to 0.004, the depths of cell used being the same as in set A. The strip corresponding to the most concentrated solution is in each case adjacent to the numbered scale.

The solutions were all blue, only the intensity of the color varying with dilution. The exposures to the Nernst lamp and spark were, respectively, 1¼ and 2½ minutes. The absorption in the ultra-violet is of course to be ascribed to the solvent, and has exactly the same limits as given under Plate 6.

In the red is a wide absorption band which in set A extends farther into the red than the panchromatic plate is capable of recording. The violet edge of the band lies at λ 5750 and is fairly sharp. The red edge was shown by visual observations to lie very close to λ 7600. In B the band has narrowed considerably, as some light is transmitted as far up in the red as λ 6200, the red edge being at approximately λ 7050. The violet edge of the band is very hazy, the transmission being greatly weakened as far towards the violet as λ 5850. The absorption shows no indication of breaking up into smaller bands as did that of cobalt chloride in acetone. Beer's law appears to hold very accurately, the absorption shown by all the strips of one set being the same.

In comparing this plate with Plate 6, it should be borne in mind that the solutions used in making this plate had almost double the concentration used in the other case. This accounts for the somewhat stronger absorption shown by the bromide. The indications are, however, that the absorbing power of the bromide in acetone is somewhat smaller than that of the chloride, which agrees with what has been noticed in the other solvents.

COBALT BROMIDE IN METHYL ALCOHOL WITH WATER. (See Plate 16.)

The concentration of cobalt bromide throughout was constant and equal to 0.088. The percentages of water, beginning with the solution whose spectrum is adjacent to the numbered scale, were 0, 0.5, 0.75, 1, 1.25, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6, 8, 10, 12.

The solution containing no water was slightly purplish in color, from which the color changed rapidly with addition of water to a pink. After 2 per cent of water had been added no appreciable change in color could be noticed by the unaided eye. The depth of absorbing layer used throughout was 2.0 cm., the exposures to the Nernst lamp and spark being 1 and 3 minutes, respectively.

The solution containing no water, and the one containing 0.5 per cent of water, show considerable absorption from λ 3900 towards the ultra-violet, which at first sight does not agree very well with what is shown by B, Plate 13. The discrepancy, however, disappears when it is noted that when the series of exposures for the spectrogram now under discussion was made, the workroom was at a temperature of about 30° C.; whereas when the negatives for Plate 13 were made the temperature was about 20° C. Cobalt bromide dissolved in methyl or ethyl alcohol is very sensitive to temperature change, a pink solution of proper concentration turning purple with a comparatively slight change of temperature. From the solution containing 0.75 per cent of water to the one containing the largest amount of water, the ultra-violet absorption recedes gradually from λ 2850 to λ 2580.

The absorption band in the green is somewhat narrower than in the solution of the chloride, but like that it narrows regularly with addition of water. Measurements on the edges of the band in the strip pertaining to the solution containing no water, give the wave-lengths λ 5050 and λ 5400, locating the center of the band at λ 5225. For the strip pertaining to the solution containing 12 per cent of water the figures are λ 5100 and λ 5300, locating the center at λ 5200. The center, therefore, shifts slightly towards the shorter wave-lengths with addition of water.

The absorption in the red was not of sufficient intensity to be registered on the photographic plates, which, accordingly, show uniform and complete transmission from λ 5500 to λ 7400.

COBALT BROMIDE IN ETHYL ALCOHOL WITH WATER. (See Plate 17.)

The concentration of cobalt bromide was constant throughout and equal to 0.088. The percentages of water, beginning with the solution whose spectrum is adjacent to the numbered scale, were 0, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6, 7, 7.5, 8, 9, 10, and 11.

The solution containing no water was blue or purplish-blue; the one containing 1 per cent of water was slightly purplish, from which the color changed very rapidly to the regular pink of cobalt solutions. No color change appreciable to the eye was noticed after the solution containing 3 per cent of water was reached.

The cell was adjusted to a depth of 2.0 cm. and the exposures to the Nernst lamp and spark were, respectively, of 1 and 3 minutes duration; the slit was, as usual, 0.01 cm. wide. The solution containing no water absorbs all light of shorter wave-length than λ 3000. The absorption recedes gradually with addition of water, and a little more rapidly at first, as is apparent from the curvature of the edge of the band nearest the scale. The solution containing 11 per cent of water transmits light of a wave-length as short as λ 2560. The green band has very nearly the same intensity as it had in the methyl alcohol solutions just described, and narrows with addition of water to about the same extent. Measurements give its center for the solution containing no water at λ 5220, and for the solution containing 11 per cent of water at λ 5200.

The absorption in the red is of a general character, showing only faint indications of bands. The whole spectrum of the solution containing no water is weak throughout the entire red region, and shows weak bands superposed upon the general absorption, having their centers at about λ 6150 and λ 6730. These regions correspond roughly to the minima of sensibility of the panchromatic plates; therefore, due allowance must be made for this in studying the spectrogram. The absorption decreases rapidly with increase in the amount of water, being practically absent in the solution containing 2 per cent. All solutions containing a greater percentage of water are completely transparent to the red as far as the limit of sensibility of the plates used.

Cobalt Bromide in Acetone with Water. (See Plate 18.)

The concentration of the colored salt throughout was constant and equal to 0.007 normal. The successive percentages of water, beginning with the solution whose spectrum is nearest the numbered scale, were 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15.

The first seven solutions were of various shades of blue, from dark to light-blue. The eighth, ninth, and tenth were light-bluish to bluish-green, after which the solutions were almost colorless, a very faint pinkish tinge only being noticed.

The depth of absorbing layer used was 2.0 cm., and the exposures to the Nernst lamp and spark lasted for 1 and 3 minutes, respectively, the slit being, as usual, 0.01 cm. wide.

As has been repeatedly observed, acetone absorbs all wave-lengths shorter than about λ 3300 for the thickness of layer here used. The edge of the band is unusually sharp, which is, however, not the case for the first eight strips of Plate 18. In fact the strip nearest the scale just barely records the line at λ 3320, the shading from this point towards λ 3800 being considerable. This shading is undoubtedly due to the effect of the colored salt. It decreases with addition of water, but is still easily noticeable in the solution containing 15 per cent of water.

Measurements on the edges of the band in the red settings being made on the limits of transmission, give the following:

Solution which contains no water, λ 5600 to beyond λ 7400
Solution containing 1 p. ct. of water, λ 5680 to beyond λ 7400
Solution containing 2 p. ct. of water, λ 5750 to beyond λ 7400
Solution containing 3 p. ct. of water, λ 5850 to λ 7400
Solution containing 4 p. ct. of water, λ 5970 to λ 7350
Solution containing 5 p. ct. of water, λ 6070 to λ 7250
Solution containing 6 p. ct. of water, absorption band broken up.

Bands are seen having their centers at λ 6160 and λ 6350, with a band extending from λ 6650 to λ 7150. In the solution containing 7 per cent of water the latter band is broken up into two, with centers at λ 6700 and λ 7000. The indications are that the band having its center at λ 6350 is really made up of two bands, the centers being at λ 6300 and λ 6430, respectively. They are, however, very faint and the slightly greater transparency near λ 6360 not very well marked. The three solutions containing the least amount of water were examined with a small, direct-vision, prism spectroscope, having a scale attached so that wave-lengths could be read off directly. These solutions were all transparent in the extreme red, the edge of the absorption band for the solution containing no water being between λ 7500 and λ 7600. It seemed extremely sharp, but this was undoubtedly due to the small dispersion of a prism spectroscope in this region of the spectrum.

Here again, as in the case of cobalt chloride in ethyl alcohol and water, we must assume that the system of narrow absorption bands is due in some way to the presence of the water, for the absorption of cobalt bromide in acetone showed no sign of breaking up into finer bands with dilution. The group of bands brought out in the bromide solution is quite different from that shown by the corresponding solution of the chloride, a fact which must be accounted for by any theory of the cobalt solutions. It will be recalled also that water added to solutions of cobalt bromide in ethyl alcohol did not break up the absorption into finer bands, as was the case with the chloride solution under similar circumstances.

COBALT NITRATE IN WATER—BEER'S LAW. (See Plate 19.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.05, 1.53, 1.02, 0.683, 0.473, 0.342, and 0.256; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For set B the concentrations were 0.683, 0.513, 0.342, 0.227, 0.158, 0.114, and 0.085; the depths of absorbing layer were the same as for A.

The most concentrated solutions were purple in color, from which the color changed to the usual pink with dilution.

The exposures to the Nernst lamp and spark lasted 1 and 3 minutes, respectively, the width of the slit used being, as usual, 0.01 cm.

The spectrogram shows two regions of absorption, one in the ultra-violet and one in the green. In A the edge of the ultra-violet band is perfectly straight and sharp, reminding one of the absorption due to acetone; the limit of transmission being at λ 3280, which is also the same as for acetone. In B the corresponding edge falls at λ 3200, but here we also find a region of transmission located at about λ 2650, increasing in width with dilution. A band of absorption is thus outlined, the limits of which are λ 2650 and λ 3200. A number of spectrograms of nitrates shows that this band is always present. It is hence connected in some way with the radical NO_3, but B makes it seem improbable that it is due to the free NO_3 ion, since the number of these in the path of the beam of light was increasing in the direction away from the numbered scale, while the absorption band narrows somewhat from strip to strip in this direction. The region of transparency beyond this NO_3 band, as we shall designate it, shows that the ultra-violet absorption of cobalt nitrate decreases with increasing dilution, when the conditions for Beer's law obtain. If it were not for the NO_3 band we should expect the ultra-violet end of transmission to look very much as it did in the case of cobalt bromide, except that in the present case it would be shifted somewhat towards the longer wave-lengths.

The absorption band in the green presents a different appearance from what it has done in the solutions already studied. In both the chloride and bromide solutions the band narrowed rapidly at first, and almost symmetrically. Here it narrows uniformly from strip to strip in A, and much more from the violet than from the red side. The result is that if measurements are made on the edges and calculations made for the position of the center of the band, this shifts continually towards the red with increasing dilution. The extreme limits of transmission in the most concentrated solution, as shown by the strip nearest the scale, are λ 4450 and λ 5500, locating the center at λ 4975. For the most dilute solution of set A the corresponding numbers are λ 4700 and λ 5450, center at λ 5075. In set B the band remains of sensibly constant width, its center falling at λ 5150.

The concentrations used in making this spectrogram were almost exactly the same as those employed in making the negatives for Plate 10, hence the two spectrograms are directly comparable. The comparison shows that for solutions of 1.5 to 2.0 normal concentration, the width of the band is approximately the same for the two salts; the band in the nitrate solution was, however, located nearer the region of short wave-lengths. As the concentration decreases the absorption of the bromide solution becomes much less than that of the nitrate solution, the band in the latter being still slightly more refrangible.

The solutions transmitted the red as far as λ 7400 without sensible absorption. Since the most concentrated solutions looked purple in the bottles, it is probable that they exerted some general absorption in the orange and red, but examination of the light transmitted through the bottles, where the layer was 5 cm. in depth, with a direct-vision spectroscope failed to reveal any definite bands in this region.

COBALT NITRATE IN WATER—MOLECULES CONSTANT. (See Plate 20.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.05, 1.67, 1.25, 0.94, 0.71, 0.55, and 0.44, the corresponding depths of absorbing layer being 3, 4, 6, 9, 13, 18, and 24 mm. The concentrations for set B were 0.55, 0.44, 0.32, 0.23, 0.17, 0.13, 0.105; the depths of cell were the same as for A. The width of slit and exposures were the same as in the case of Plate 19.

In A the ultra-violet transmission is limited by the red edge of the NO_3 band. In the present case this band widens somewhat with decreasing concentration, the limits of transmission being λ 3280 and λ 3330 for the most concentrated and most dilute solutions, respectively. In B there is some transmission beyond the NO_3 band, the violet limit of the transmitted region remaining unchanged with dilution. This is exactly the same as was found with cobalt bromide when molecules were kept constant. This ultra-violet absorption does not vary with dilution, indicating that it might be a property of the molecules of the dissolved salt. The NO_3 band, however, widens quite perceptibly with dilution, its limits (transmission) in the most concentrated solution of B being λ 2800 and λ 3150, while the corresponding figures for the most dilute solution are λ 2700 and λ 3230.

The green band in A widens, though not uniformly, with decrease in concentration. The edges for the most concentrated solution are at λ 4550 and λ 5500, and for the most dilute solution λ 4450 and λ 5600, respectively. It appears, therefore, that for this range of concentrations the widening is symmetrical, the center of the band remaining approximately at λ 5000. In B the band also widens, but somewhat unsymmetrically, the violet edge being displaced much more than the red edge. The center of the band for the most dilute solution is at λ 5175. The red is freely transmitted to beyond λ 7400.

COBALT SULPHATE IN WATER—BEER'S LAW. (See Plate 21.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.65, 0.52, 0.41, 0.33, 0.26, 0.20, and 0.16; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. For set B the concentrations were 0.26, 0.20, 0.16, 0.13, 0.10, 0.08, and 0.06; the depths of cell were the same as for set A. The slit was adjusted to a width of 0.01 cm. and the exposures to the Nernst lamp and spark lasted for 1 and 2 minutes, respectively.

The solutions have only one absorption band, namely the one in the green. In the ultra-violet they are perfectly transparent, the last lines in the comparison spectrum showing with the same intensity through the cell containing the solution. In the red they transmit freely light of all wave-lengths as far up as λ 7400.

The band in the green has exactly the same width and position in all the strips belonging to the solutions of one set; hence, Beer's law holds rigidly. In set A the extreme limits of transmission are λ 4900 and λ 5400. The shading of the violet edge is great, extending somewhat below λ 4500. The red edge is somewhat sharper, although not as much so as would appear from the spectrogram. The increasing sensibility of the Seed film with wave-length in the region of λ 5400 makes this edge appear much sharper than it really is.

A comparison of the seventh strip (counted from the scale) of A with the seventh strip of B, Plate 3, shows that for a concentration of 0.16 normal, the absorption of the sulphate is slightly greater than for the chloride; as the chloride deviates from Beer's law, while the sulphate solutions do not. We may say that, for a certain range of concentrations greater than 0.2 normal, the absorbing power of solutions of the chloride and sulphate is the same in the green; for greater concentrations the chloride exerts stronger absorption, while for more dilute solutions the absorption of the sulphate solutions is greater. A comparison of Plate 19 B shows that the absorption band in the green is of sensibly the same width, while the concentration of the nitrate solution pertaining to the seventh strip was about 40 per cent greater than that of the corresponding sulphate solution. As the sulphate dissociates less strongly than the nitrate or chloride, it does not seem altogether reasonable to ascribe the green band to the cobalt ions.

Since Beer's law holds so accurately for the sulphate solutions, it was evidently unnecessary to study sets of solutions of such concentrations as to give a constant number of ions, or a constant number of molecules. In the former case we should get a marked narrowing of the band and in the latter case a widening.

COBALT SULPHOCYANATE IN WATER—BEER'S LAW. (See Plate 22.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.17, 1.62, 1.08, 0.72, 0.50, 0.36, and 0.27, the corresponding depths of cell being 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.36, 0.27, 0.18, 0.12, 0.083, 0.060, and 0.045; the depths of absorbing layer were the same as in set A.

The color of solutions of the sulphocyanate is much deeper than of solutions of other salts of cobalt used in the present work. The most concentrated solutions were very deep purple, from which, as concentration decreased, the color changed to the usual pink. The exposures to the Nernst lamp and spark were, respectively, 1⅓ and 3 minutes, the slit being adjusted to a width of 0.01 cm.

The spectrogram shows a region of strong absorption in the ultraviolet, which narrows rapidly with dilution, the limit of transmission for the most concentrated solution in A being λ 3630, while for the most dilute solution it is λ 3370. The corresponding wave-lengths for B are λ 3240 and λ 3130.

The absorption band in the green is very wide in A, extending in the case of the most concentrated solution from λ 4300 to λ 6350, and in the most dilute from λ 4350 to λ 5700. The violet edge moves towards the red slowly but uniformly with dilution, while the red edge moves in the opposite direction very rapidly from the first to the third solution, then more slowly. There is apparently a band in the red not resolved from the green band, which disappears very rapidly with dilution, and which causes the apparent rapid narrowing of the green band observed in the spectrogram.

In B the green band also narrows considerably, its limits in the first solution being λ 4900 and λ 5430, and in the seventh solution λ 5050 and λ 5320. The violet edge of the band is shaded considerably in the first three solutions; the transmission being incomplete as far as λ 4500. In the red this set of solutions does not show any absorption sufficiently intense to be recorded on the photographic plate.

A comparison of the fourth strip of B, Plate 22, with the fourth strip of B, Plate 3, shows that the green band on the two has about the same intensity and width. The depth of the two corresponding solutions was the same, but the concentration of the chloride solution was 0.329, while that of the sulphocyanate was only 0.12. This would indicate for the sulphocyanate solution an absorbing power about 2.5 times as great as for the chloride solution, considering only the green band. It is also worth noticing that whereas the green band in the chloride solutions remains practically constant for concentrations below 0.4 normal, when the conditions for Beer's law are fulfilled, the same band in the sulphocyanate solutions continues to narrow rapidly, even where the concentration is as small as 0.05 normal. The percentage dissociation of solutions of the two salts having equal concentrations is not very different in amount.

Cobalt Sulphocyanate in Water—Molecules Constant. (See Plate 23.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.17, 1.78, 1.34, 1.01, 0.78, 0.62, and 0.51; the corresponding depths of absorbing layer were 3, 4, 6, 9, 15, 18, and 24 mm. For B the concentrations were 0.51, 0.40, 0.30, 0.215, 0.165, and 0.10; the depths of cell were the same as for A. The exposures to the Nernst lamp and the spark were, respectively, 1½ and 3 minutes, the width of slit being 0.01 cm.

The ultra-violet absorption still narrows quite markedly with dilution, the limits of transmission for the most concentrated and most dilute solutions of A being λ 3630 and λ 3430; the corresponding limits for B were λ 3290 and λ 3220. There is, then, a tendency for this band to remain constant in width as the dilution is increased, since the narrowing is very much less in B than in A.

The green band widens somewhat, though less than in the case of some of the other cobalt solutions studied. In A the widening of this band towards the violet and the narrowing of the ultra-violet absorption produce the curious result that a rather narrow region of transmission moves continuously towards the ultra-violet with dilution, its width remaining sensibly constant. By varying the depth of layer the transmission may be made to have almost any width desired.

The limit of the violet edge of the band in A changes from λ 4350, in the most concentrated solution, to λ 4220 in the most dilute. The red edge is at λ 6400 in the first solution. It moves rapidly towards the shorter wave-lengths at first, reaching λ 5900 in the fifth solution. From this point it moves gradually towards the red with further dilution. The apparent narrowing of this band at first is undoubtedly due to the band located in the red, which disappears rapidly with dilution. If this band were absent we should find that the green band would widen continuously, though slowly, with decrease in concentration when molecules are kept constant.

In B the limits of the green band in the most concentrated solution are λ 4630 and λ 5500, while in the most dilute solution they are λ 4580 and λ 5520, thus showing a widening of about 70 Ångström units. The widening is somewhat unsymmetrical, which is to be explained, however, by the lack of uniformity in the sensibility of the Seed plate in the region occupied by the red edge of the band.

A comparison of the first strip of B with the first strip of Plate 20 A shows that the width of the green band in the two is very nearly the same. The depth of cell used was 3 mm. in each case, but the concentration of the nitrate was 2.05 while that of the sulphocyanate was only 0.51, indicating an absorbing power for the sulphocyanate nearly 4 times as great as for the nitrate.

COBALT ACETATE IN WATER—BEER'S LAW. (See Plate 24.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is nearest the numbered scale, were 0.86, 0.68, 0.54, 0.43, 0.34, 0.27, and 0.22; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.34, 0.25, 0.21, 0.17, 0.14, 0.11, and 0.09; the depths of cell were the same as in A. The color of the solutions changed from purplish to the usual pink with increasing dilution. The exposures to the Nernst lamp and spark were 1 and 2 minutes respectively, the slit having a width of 0.01 cm. as usual.

The absorption in the ultra-violet is slight, and decreases with decrease in concentration. The limits of transmission for the most concentrated and most dilute solutions of set A are λ 2620 and λ 2470, and for set B λ 2470 and λ 2390. Some irregularities in the intensities of the various spark spectra are noticed, indicating considerable fluctuations in the intensity of the spark during the different exposures. In spite of this there can be no doubt that the spectrogram shows an increase of transparency with decreasing concentration.

The green band narrows with dilution, but more and more slowly as the concentration is diminished. In the last three or four solutions of set B it remains practically constant. The limits of transmission for the most concentrated and the most dilute solutions of set A are λ 4500 and λ 5600, and λ 4600 and λ 5520, respectively, placing the center of the band at about λ 5050 throughout. In set B the center is near λ 5175. A part of this change in position may, however, be accounted for by the lack of uniformity in the sensibility curve for the Seed film. From the red edge of the green band the solutions transmit freely light of all wavelengths as far as beyond λ 7400.

Strip 1 of A may be compared with the first strip of Plate 11 A, and it will be found that the width of the green band in the two is very nearly the same. The depth of the absorbing layer in each case was 6 mm., but the concentration of the bromide solution was 1.51, while that of the acetate was 0.86; thus showing that the acetate solution absorbs green light much more strongly than a solution of the bromide having the same concentration. A comparison of the seventh strip of A with the seventh strip of Plate 23 B shows that the green bands in the two agree almost exactly in width and position. The depth of the cell in each case was 24 mm., while the concentrations of the sulphocyanate and acetate were, respectively, 0.10 and 0.22. This indicates that the sulphocyanate solution has about double the absorbing power of the acetate solution of equal concentration, for green light.

GENERAL SUMMARY OF RESULTS WITH COBALT SALTS.

We shall consider the aqueous solutions first, since they are the simplest from the standpoint of the absorption spectra. All of the solutions studied, with two exceptions, at room temperatures and with such depths of absorbing layer as were employed, show only two regions of absorption, one in the ultra-violet and one in the green. The exceptions are the concentrated solutions of the sulphocyanate, and the solutions of cobalt bromide to which large amounts of calcium bromide had been added; both of which show some absorption in the red.

Let us first consider the absorption in the ultra-violet. Solutions of all the salts studied, except the sulphate, have a region of so-called one-sided absorption, which cuts off more or less of the ultra-violet end of the spectrum, depending upon the salt used. In all cases the band narrows with dilution when the conditions for Beer's law obtain, but tends to remain approximately of constant width when molecules are kept constant. In the bromide and nitrate the band is constant with molecules constant. This indicates that the absorber which is responsible for this band is in every case the undissociated molecule, and to account for the deviations from constancy in the band when the number of absorbers is kept constant we may assume that the molecules in concentrated solutions associate to some extent, and that their absorbing power is thereby increased; or we may assume that with increasing dilution they become more and more hydrated, and that this decreases their absorbing power. A choice between these two explanations can not be made without a further study of the subject.

In addition to the one-sided ultra-violet band, cobalt chloride has a band at λ 3300, which disappears rapidly with dilution even when molecules remain constant. This band seems to increase in intensity very rapidly with rise in temperature. We can not very reasonably ascribe this band to the undissociated molecules as such, since it not only narrows rapidly but entirely disappears when these are kept constant. To explain it we must hence look to either association or hydration. It may be remarked here that by association we do not mean simply a grouping together of similar particles, but also a grouping together of such parts as molecules and ions, or aggregates of molecules and ions, etc. The term association, therefore, includes the complex anions assumed to exist by Donnan and Bassett. Both association and hydration are known to diminish with rise in temperature (except Donnan and Bassett's complex anions); with increasing concentration at a given temperature association is known to increase while hydration decreases. In a fairly dilute solution the amount of association is perhaps negligible. If we then assume that the λ 3300 band is due to some aggregate, this would explain its disappearance on dilution, since this process destroys the aggregate. But raising the temperature also destroys the aggregate without, however, causing the absorption band to disappear. The fact is that it becomes more intense as the temperature rises. It seems, therefore, rather difficult to assume that it is due to aggregates, at least to aggregates which are not abnormal in their behavior.

If we assume that the band is due to some *relatively simple hydrate* the facts are at once accounted for, since with rise in temperature complex hydrates break down into simpler ones. Also with increase in dilution more and more complex hydrates are formed, which would also cause the band to disappear.

The green band appears in all aqueous solutions, although with various intensities and apparently with somewhat different positions. The change in position is inappreciable in the case of dilute solutions, and with concentrated solutions it depends entirely upon whether the band widens symmetrically or not. In general, it widens perhaps a trifle more towards the violet, especially at first. A very slight amount of general absorption will shift the apparent center of an unsymmetrical band, and this is perhaps the explanation of the slight variation in the position of the center of this band in concentrated solutions of different salts.

The intensity of the band as indicated by its width on the photographic plate is more interesting. For if it is due to the cobalt cation as such, it ought to have a greater intensity in solutions which are strongly dissociated than in slightly dissociated solutions, concentration and depth of layer being constant.

The spectrograms of this chapter show the following: For solutions which have a concentration of 2 normal or more, the salts arranged in the order of increasing intensity of the green band are, nitrate, bromide, chloride, sulphocyanate. For dilute solutions (concentrations of about 0.1 or 0.2 normal) the order is, bromide, chloride, nitrate, sulphate, acetate, sulphocyanate. Arranged in the order of increasing dissociation the salts would be acetate, sulphate, sulphocyanate, nitrate, chloride, bromide, which is just the opposite of the order of increasing intensity of the green band, if we leave out the sulphocyanate. It is very evident, therefore, that something besides the cobalt cation must play a part in the production of this band.

Plate 21 shows that when the concentration of the sulphate is varied from 0.65 to 0.06 the width of the band does not vary, provided the light is made to pass through such depths of the solution that the product of concentration and depth remains constant; it follows, therefore, that in this case the absorption is simply proportional to the number of cobalt atoms in the solution, and independent of whether these exist as ions, combined with SO_4, as molecules, or as parts of the various aggregates or hydrates that we may assume to exist in the solution. The same is approximately true for the nitrate solutions, although in this case there is a slight narrowing of the band, indicating that the absorbing power of the various "absorbers" is not the same. In general, the simplest explanation of the green band is to assume, as we have just done, that the cobalt atom, no matter what it is combined with, has the power of absorbing green light, the intensity of the absorption depending, however, upon the nature of the combination.

In the red, aqueous solutions show little or no absorption unless they are very concentrated, or are at a high temperature, or have relatively large amounts of such substances as HCl, $CaCl_2$, or $AlCl_3$, etc., added to them. Whether the absorption produced by these different methods is the same or not for any given salt can not yet be answered definitely. We have already pointed out (see page 23) that the absorption of a solution of cobalt bromide to which a large amount of calcium bromide is added is similar *but not identical* with that of a solution of the chloride of cobalt to which a large amount of calcium chloride had been added. The work of Jones and Uhler ("Hydrates in Aqueous Solution") indicates that the absorption of cobalt chloride when "dehydrated" with calcium chloride, aluminium chloride, or calcium bromide, is the same, but that this differs somewhat from the absorption of very concentrated solutions of cobalt chloride alone. In the latter case only three of the five bands were seen, and these were located nearer the red end of the spectrum; but the "displacement" was different for different bands, amounting to 170 A.U. for the least refrangible, and 115 A.U. for the most refrangible.

The entire absence of this red absorption in solutions of moderate concentration shows at once that it can not be accounted for by the simple theory of dissociation, according to which there should be present only ions and molecules. The fact that the absorption does appear in *very concentrated solutions* naturally suggests that it may be due to aggregates of molecules, but this view is not tenable, since the absorption increases with rise in temperature. The most reasonable explanation, and the one that best fits the facts, is that it is due to some relatively simple hydrate of the molecule. The conditions which favor the formation of a "simple" hydrate are high temperature, or great concentration, or the addition of large amounts of some dehydrating agent to a moderately concentrated solution, and in all of these cases the absorption in the red appears. That this explanation is the correct one is also made probable by the work of Russell on the absorption of the various dry salts of cobalt. The anhydrous salts all show absorption in the red, as do also the simple hydrates; while hydrates containing 6 molecules of water exert no absorption in this region of the spectrum.

In non-aqueous solvents only the chloride and bromide have been studied. The chloride, which in aqueous solutions showed an absorption band near λ 3300, has in the alcoholic solutions two bands, one at λ 3100 and the other at λ 3600. These bands behave very much like the λ 3300 band in the aqueous solution, disappearing quite rapidly with dilution. They are most likely due to some relatively simple solvate. A study of the change of absorption with temperature will undoubtedly throw some light on this point.

The green band is present in all the non-aqueous solutions studied, although its intensity in the acetone solutions is so small that very deep layers of solution were necessary in order to see even a trace of it. This is exactly what we should expect if the view is held that the cobalt atom, no matter with what it is associated, absorbs green light to some extent. The intensity of the band diminishes as we pass from solutions in methyl alcohol to those in ethyl alcohol and acetone, but so do the concentrations; hence, as in aqueous solutions, the intensity of the band may be said to be roughly proportional to the concentration.

In the red the absorption is much more intense in the non-aqueous than in aqueous solutions, the intensity for equal concentrations increasing very rapidly as we pass from methyl alcohol to ethyl alcohol to acetone.

The structure of the band differs materially in the different solvents, as has been pointed out in the description of the spectrograms. With dilution it narrows rapidly in methyl alcohol, slower in ethyl alcohol, and remains constant or nearly so in acetone. That these changes can not be explained by dissociation has already been pointed out by Jones and Uhler, who suggested that they may be due to **solvation**. This is altogether reasonable, and the behavior of the spectrum is exactly what we should expect from the conclusions arrived at in the discussion of aqueous solutions. The red absorption then was ascribed to "simple" hydrates, such as contain 2 or 3 molecules of water or less. It is not unlikely that "simple" solvates of cobalt salts, in general, have this property of absorbing red light.

We should expect the power to form solvates to be greater for methyl alcohol than for ethyl alcohol, and greater for the latter than for acetone. Hence, in case of ethyl alcohol and acetone at ordinary temperature, all the solvates formed are perhaps simple enough to exert powerful red absorption, while with methyl alcohol this is only the case with concentrated solutions or at elevated temperatures. The differences in the structure of the band in the different solvents are, of course, to be expected, since the "absorbers" are different.

CHAPTER III.

SALTS OF NICKEL.

Among the more important investigations on the absorption spectra of nickel salts are the following:

Brewster,[1] in his early work on absorption, included the nitrate of nickel, and Emsmann [2] also studied the same salt.

Vogel [3] studied not only cobalt chloride but also the chloride of nickel, in connection with its power to absorb light.

The work of Soret [4] in 1878 also had to do with the chloride of nickel.

The splendid investigations of Hartley[5] on absorption spectra included also certain salts of nickel.

The work of Müller [6] in connection with salts of nickel calls for special comment. He tested Beer's law for certain salts of nickel and copper, and found that it holds for the sulphate and nitrate of nickel. The chloride and bromide of nickel showed deviations from the law. The deviations from Beer's law he thinks are to be explained on the basis of dissociation.

In a subsequent paper Müller [7] tests the above suggestion, and comes to the conclusion that dissociation alone can not account for all the deviations from Beer's law. If the law does not hold, rise in temperature would produce a change in the absorption, and rise in temperature would be expected to produce a result similar to increase in concentration.

The fact is that *rise in temperature produces a different effect on absorption from increase in concentration,* which shows that more than one factor must be taken into account in dealing with the causes of the deviation from Beer's law.

Müller thinks that both hydration and molecular complexes come into play.

NICKEL CHLORIDE IN WATER—BEER'S LAW. (See Plate 25.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.66, 2.00, 1.33, 0.89, 0.61, 0.44, and 0.33, the corresponding depths of layer being 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.44, 0.33, 0.22, 0.15, 0.101, 0.073, and 0.055; the depths of layer were the same as for A.

The solutions were green; the more dilute ones tending towards a light yellowish-green. The exposures to the Nernst lamp and spark were 1⅛ and 3 minutes, respectively, the slit having a width of 0.01 cm.

---

[1] Phil. Mag. (4), 24, 441 (1862).

[2] Pogg. Ann. Erganzb., 6, 334 (1875).

[3] Ber. d. deutsch. chem. Gesell., 8, 1533 (1875).

[4] Archiv. d. Sci. Phys. et Nat., 61, 322 (1878).

[5] Trans. Roy. Dub. Soc. (2), 7, 253 (1900). Journ. Chem. Soc., 83, 221 (1903).

[6] Ann. d. Phys., 12, 767 (1903).

[7] Ibid., 21, 515 (1906).

A shows three regions of absorption, one in the extreme ultra-violet, a band in the end of the visible violet, and a band cutting off the extreme red. Besides this there is a rather strong general absorption in the entire ultra-violet, beyond the absorption band in the end of the violet.

The extreme ultra-violet absorption perhaps narrows slightly with dilution, although from the second strip to the seventh the limit of transmission seems to remain almost fixed at λ 2550. The first solution, however, shows much more absorption in the whole ultra-violet region, including the band at λ 3960.

The band at λ 3960 narrows from the first to the third strips (counting from the scale) and then remains of constant width, the limits of transmission being approximately λ 3700 and λ 4230. The scale in the reproduction is shifted towards the red by nearly 50 A.U., due to the fact that in making the prints this was adjusted with reference to the narrow comparison strip seen at the top of the spectrogram. This strip is displaced, as may be seen by comparing the spark lines in the ultra-violet. The scale for the red end of the plate is, however, correctly placed, so there is a slight discrepancy at the point where the two prints were joined together.

The absorption in the red shades off very gradually through a range of wave-lengths of about 1000 A.U., being quite noticeable on the negative at λ 6100 in the strip corresponding to the most concentrated solution, and at λ 6200 in the strip corresponding to the most dilute solution. The limits of transmission for the two strips are at λ 7150 and λ 7250, respectively. These measurements indicate a slight narrowing of the absorption band with dilution, but it must be remembered that photographic registering of the spectra is not the best method for studying such very hazy absorption bands, since a very slight change in the length of exposure, or intensity of the source of light used, may apparently shift the band very markedly. The only satisfactory method for studying such cases of hazy absorption is a spectrophotometric determination of the absorption coefficient for a number of wave-lengths in the region.

In B the absorption in the extreme ultra-violet has disappeared, the last lines in the spark showing as well in the strips taken through the solutions as in the narrow comparison strip with nothing but air in the path of the beam of light.

The band at λ 3960 has become faint, but still shows distinctly on the negative. It remains unchanged in intensity in the seven strips on the spectrogram.

The absorption in the red, although present as shown by the green color of the solutions in their bottles, was of too diffuse a character to be registered on the photographic plate, which, hence, shows complete transmission to beyond λ 7400. On the whole, except for the most concentrated solution, Beer's law seems to hold quite accurately for nickel chloride.

Nickel Chloride in Water—Ions Constant. (See Plate 47 A.)

The concentrations, beginning with the solution corresponding to the strip nearest the numbered scale, were 2.66, 0.93, 0.51, 0.305, 0.200, 0.135, 0.095; the depths of cell were 3, 4, 6, 9, 13, 18, and 24 mm. The exposures were 1 and 3 minutes for the Nernst lamp and spark, respectively, the width of the slit being 0.01 cm.

The spectrogram shows exactly what might be expected from a study of Plate 25. The extreme ultra-violet absorption disappears rapidly, as does the absorption in the red. The band at λ 3960, very wide at first, narrows rapidly, becoming very faint in the most dilute solution.

This plate, together with the similar one for cobalt chloride (Plate 39 B), shows at a glance what an insignificant rôle ions play in producing the absorption of solutions of cobalt and nickel salts.

Nickel Chloride in Water—Molecules Constant. (See Plate 26.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.66, 2.18, 1.63, 1.22, 0.935, 0.750, and 0.610; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For set B the concentrations were 0.800, 0.660, 0.493, 0.365, 0.280, 0.220, and 0.160; the depths of the cell were the same as for set A. The exposures were 1 and 3 minutes, respectively, for the Nernst lamp and spark, the slit having a width of 0.01 cm.

The general ultra-violet absorption beyond the λ 3960 band seems to remain nearly constant in the five most concentrated solutions of set A, then increases markedly in the sixth and seventh. The λ 3960 band narrows slightly from the first to the second strip (counting from the scale), then begins to widen, slowly at first, but more rapidly from the fifth to the seventh solutions.

In B the general ultra-violet absorption may still be seen, and it increases with dilution. The λ 3960 band also widens regularly with dilution. In the red the absorption increases regularly with dilution in both A and B.

Nickel Chloride in Water with Calcium and Aluminium Chlorides. (See Plate 27.)

The concentration of nickel chloride throughout was constant and equal to 0.372. The concentrations of calcium chloride, beginning with the solution whose spectrum is adjacent to the numbered scale, were 3.97, 3.40, 2.85, 2.30, 1.75, 1.20, 0.64, and 0.00. The corresponding concentrations of aluminium chloride were 2.61, 2.25, 1.88, 1.52, 1.16, 0.79, 0.43, and 0.00.

A is the spectrogram made with the solutions containing calcium chloride, while B was made with those containing the aluminium chloride. The two spectrograms may conveniently be described together, as this will facilitate comparisons. The strips will be referred to as first, second, third, etc., the number giving the position of the strip with reference to the numbered scale.

In general it may be stated that the absorption in the violet and ultra-violet is somewhat greater for the solutions containing aluminium chloride than for the corresponding ones containing calcium chloride. This is partly due to the greater absorption of the aluminium salt *per se* for ultra-violet light. (See "Hydrates in Aqueous Solution," Plate 11 A.) The first strip of A shows that transmission in the violet ceases at λ 4320, and that there is a slight return to transparency at λ 3000 to λ 3100, then complete absorption to λ 2200 or the end of the spectrum. The λ 3960 band narrows regularly with curved edges as the concentrations of the calcium salt decrease, its limits in the eighth strip being λ 4150 and λ 3750. The increase of transparency beyond the band is also very marked.

The first strip of B shows that transmission in the violet ceases at λ 4370, and that there is no return to transparency in the ultra-violet. The red edge of the λ 3960 band moves towards the region of shorter wave-length, rapidly in the first four strips, then more slowly till the eighth strip is reached, where the limit of transmission is λ 4150 as in A. No transmission in the ultra-violet region beyond the band is visible in the first three strips. In the fourth strip there is a slight amount of transmission from λ 2800 to λ 3400, which increases rapidly as the amount of aluminium chloride is further diminished.

The red end of A shows that, although the limit of transmission moves slightly towards the region of longer wave-lengths with decrease in the amount of calcium chloride, the absorption in the region λ 6000 to λ 6500 increases rapidly, thus showing that on the whole the absorption in the red is decreased very much by adding the calcium salt.

With the addition of aluminium chloride the absorption in the region λ 6000 to λ 6500 decreases slightly, while in the region λ 6800 to λ 7100 it increases considerably; on the whole, therefore, the red absorption is perhaps somewhat increased.

The first three solutions show three rather narrow absorption bands, whose wave-lengths are λ 6110, λ 6250, and λ 6440. Of these the first and last are rather faint, the one at λ 6250 fairly intense. They could not be seen in a layer of the mother-solution of aluminium chloride 20 cm. deep, and hence are not to be ascribed to the aluminium salt. A careful examination of the first strip on the negative for A reveals faint traces of the three bands, having here about the same intensity as they have in the second strip of B. The bands are hence to be ascribed to the nickel salt. A more concentrated solution of the nickel salt with large quantities of the dehydrating agents would undoubtedly have brought out these bands very much better.

NICKEL SULPHATE IN WATER—BEER'S LAW. (See Plate 28.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.1, 1.7, 1.32, 1.05, 0.80, 0.65, and 0.53; the corresponding depths of absorbing layer being 6, 7.5, 9.5, 12, 15, 19, and 24 mm. The concentrations for set B were 0.80, 0.64, 0.50, 0.40, 0.32, 0.25, and 0.20; the depths of cell were the same as in A. The exposures to the Nernst lamp and spark lasted 1 and 2 minutes, respectively, the slit having a width of 0.01 cm.

The spectrogram shows that the solutions were quite transparent in the ultra-violet. That there is a slight amount of general absorption beyond the λ 3960 band may, however, be inferred from the fact that although the exposure for the narrow comparison strip was only about one-fourth as long as that for the spark spectrum in the strips, the former has about the same intensity as the latter. Also the extreme ultra-violet lines shown by the comparison strip do not appear in the spark spectrum transmitted through the solutions; which indicates the presence of a band in the region below λ 2350.

The λ 3960 band has exactly the same width in all the strips, corresponding to the solutions of either A or B, showing that Beer's law holds exactly. The limits of transmission in A are λ 3600 and λ 4320, and in B λ 3700 and λ 4250, which gives the center of the band in A at λ 3960 and in B at λ 3975.

In the red A shows complete absorption beyond λ 6400, and very strong shading from λ 6400 to λ 5900. Indications are that the absorption in this region decreases very slightly with dilution. B shows faint transmission to λ 7400, with rather strong shading from λ 6100. No appreciable change in the absorption with dilution can be noted from the spectrogram. A comparison of the seventh strip of B with the seventh strip of A, Plate 25, shows that the width of the λ 3960 band, as shown by the two, is almost exactly the same. The depth of cell in both cases was 24 mm., but the concentration of the chloride solution was 0.33, while that of the sulphate was only 0.20. This indicates a greater absorbing power for the sulphate in this region of the spectrum. A comparison of the red ends of the same strips shows that the sulphate solution absorbs the red much more intensely than the chloride.

NICKEL ACETATE IN WATER—BEER'S LAW. (See Plate 29.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.50, 0.40, 0.31, 0.25, 0.20, 0.15, and 0.13; the corresponding depths of cell were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. For B the concentrations were 0.20, 0.16, 0.13, 0.10, 0.08, 0.06, and 0.05; the depths of cell were the same as in A. The exposures to the Nernst lamp and spark lasted for 1 and 2 minutes, respectively, the slit having a width of 0.01 cm.

There is evidence of a band in the extreme ultra-violet, the limit of transmission in A being λ 2400. The general absorption in the region between this and the λ 3960 band is not very strong, due to the comparatively small concentration of the solutions used.

The λ 3960 band narrows somewhat with dilution in A, the fifth, sixth, and seventh strips showing slight transmission even at its center. In B the band has become faint, though still showing distinctly. It remains of sensibly the same intensity with dilution. In the red A shows some transmission as far as λ 7400, with shading from about λ 6600. In B the red absorption was too faint and diffuse to be registered on the photographic plate.

A comparison of the seventh strip of A with the seventh strip of Plate 26 B shows that although the absorption of the acetate is somewhat greater it is not very much so. The depth of absorbing layer used in making the two strips was the same, namely 24 mm., but the concentration of the chloride was 0.16 while that of the acetate was only 0.13. Hence, the absorbing power of the acetate solution is greater than that of the chloride. A direct comparison of the absorption of the acetate and sulphate solutions is not possible from the spectrograms, since the concentrations differed too much; but the indications both from the comparison with the chloride and from visual observations in the red are that the two absorb about the same if concentration and depth of layer are equal.

The absorption bands of nickel salts seem to be very similar in their behavior to the green band of cobalt. In our study of that band we came to the conclusion that the absorbing power for green light is a property of the cobalt atom, which is only slightly affected by its immediate surroundings. Similarly, it appears from our study of nickel salts that the absorption shown by them is a property of the nickel atom, and there are only a few hints that it is changed very much by the immediate surroundings.

One of these is the marked widening of the λ 3960 band in nickel chloride as we approach a saturated solution. Others are the widening of the same band when large quantities of calcium or aluminium chlorides are added, and the appearance of the narrower bands in the orange and red, together with the change in the general absorption there under the same conditions. These point to the fact that the simplest hydrates have a somewhat different absorption from the more complex ones, all of which (if there are several) seem to have about the same action on light. More definite conclusions on this subject must be deferred until the investigation shall have been extended to more compounds and under more varied conditions.

CHAPTER IV.

SALTS OF COPPER.

A number of investigators have included salts of copper among those whose absorption spectra they have studied. The results obtained with copper salts are, however, neither as interesting nor apparently as important as those furnished, for example, by cobalt.

Hartley [1] in his elaborate investigations on absorption spectra included the chloride and bromide of copper; and Müller,[2] in his discussion of the deviations from Beer's law, dealt with the salts of both copper and nickel. Hartley explained the color changes in the case of copper chloride on addition of water as due to the formation of the compounds $CuCl_2,H_2O$ and $CuCl_2,2H_2O$ from the compound $CuCl_2$.

Donnan and Bassett,[3] in their interesting paper in which they develop the conception of complex ions as the cause of certain color changes in solution, also include cupric chloride.

Knoblauch [4] also studied the absorption spectra of copper sulphate.

We have included in our work certain of the salts of copper, which seemed to be most promising.

Copper Chloride in Water—Beer's Law. (See Plate 30.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 4.5, 3.37, 2.25, 1.50, 1.038, 0.750, and 0.562; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 1.5, 1.12, 0.75, 0.50, 0.37, 0.25, and 0.19; the depths of cell were the same as in A. The concentrated solutions as viewed in their bottles were green. With dilution the color changed through greenish-blue to a rather light-blue. The exposures to the Nernst lamp and spark were, respectively, 1½ and 3 minutes, the slit having a width of 0.01 cm.

The spectrogram shows two regions of absorption, one in the blue, violet, and ultra-violet, and the other in the red. The two are evidently of quite different character, since the former narrows very rapidly with decrease in concentration, the other only slightly.

In A the first strip shows that transmission ends at λ 4750, while for the seventh strip the limit is at λ 3750. The change in absorption is most rapid from the second to the fifth strips, giving the edge of the band the form of a compound curve. In B the band narrows most rapidly from the first to the fourth strips, the corresponding limits of transmission being λ 3950 and λ 3400. In the seventh strip transmission ceases at λ 3250.

The edge of this ultra-violet band is fairly well-defined throughout, differing in this respect from that of the red band, which is somewhat hazy, although much less so than was the case with the red band of nickel.

---

[1] Trans. Roy. Dublin Soc. (2), 7, 253 (1900).

[2] Ann. d. Phys., 12, 767 (1903).

[3] Journ. Chem. Soc., 81, 955 (1902).

[4] Wied. Ann., 43, 738 (1891).

In the red the first strip of A shows complete absorption from λ 5900 to the end of the spectrum. The seventh strip shows transmission as far as λ 6150. The corresponding readings for the first and seventh strips of B are λ 6450 and λ 6675. The edge is, however, very indefinitely defined in B, the shading being considerable.

It appears, therefore, that the red band also narrows with dilution, although much less than the ultra-violet one. It also narrows more rapidly at first, giving the edge of the band a curved form, concave towards shorter wave-lengths. At great dilutions and correspondingly deep layers of solution, the edge of the band would in all probability be straight, and perpendicular to the length of the strips.

Copper Chloride in Water—Molecules Constant. (See Plate 31.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 4.53, 3.59, 2.63, 1.97, 1.50, 1.19, and 0.97; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 1.50, 1.22, 0.91, 0.68, 0.52, 0.415, and 0.335; the depths of cell were the same as for A. The exposures to the light of the Nernst lamp and spark lasted, respectively, 1½ and 3 minutes, the width of the slit being 0.01 cm.

In this spectrogram we find that the absorption band in the ultraviolet still narrows rapidly, while that in the red shows a tendency to widen with dilution. The limits of transmission shown by the first and seventh strips of A are λ 4750 and λ 4100, with the edge showing a compound curve similar to the one in Plate 30 A, but with less curvature. For the first and seventh strips of B the limits are λ 3990 and λ 3500, the edge forming a curved line convex towards the region of short wavelengths. In the red, the first strip of A gives the limit of transmission as λ 6050. In the second and third strips the limit is a little farther up in the red, being near λ 6075. In the fourth strip it is again at λ 6050, from which it moves gradually towards shorter wave-lengths until the seventh strip is reached, where it is at λ 5975. The edge of the band is hence curved, with the convex side towards the longer wave-lengths.

In B the band widens continuously with decreasing concentration, the limit of transmission for the solution pertaining to the first strip being λ 6500, while the seventh strip shows complete absorption at λ 6400. The edge is not sharply defined, the shading extending as far as λ 5000 with considerable intensity. From λ 6000 to λ 5950 the blackening of the negative increases very rapidly, and this position of most rapid increase in transmission seems to be sensibly the same for all the solutions of the one series. This is also nearly the position of the limit of transmission for the concentrated solutions used in A, and also in Plate 30 A. Hence, it seems likely that this is the real limit of the absorption band.

Copper Chloride in Methyl Alcohol—Beer's Law. (See Plate 32.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.744, 0.595, 0.469, 0.372, 0.297, 0.233, and 0.186; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. For B the concentrations were 0.233, 0.186, 0.147, 0.116, 0.093, 0.073, and 0.058; the depths of absorbing layer were the same as in set A.

The solutions were all green, the intensity of the color only changing with dilution. Exposures to the light of the Nernst lamp and spark lasted for 1½ and 3 minutes, respectively, the slit having the usual width of 0.01 cm.

As in the aqueous solutions we have two regions of absorption, one in the blue, violet, and ultra-violet, the other in the red. Both regions contract somewhat on decreasing the concentration of the solutions, but the one in the violet region contracts much more than the one in the red.

The limit of transmission for the first strip in A is at λ 4800, while for the seventh strip it is at λ 4630. The edge of the band forms a line which is slightly curved at first, the concave side being towards the violet. From the third to the seventh strips the edge forms a line which is sensibly straight. In B the limit of transmission for the first strip is λ 4420, while for the seventh it is λ 4200, the edge forming a line which is very nearly straight. From the fourth to the seventh a slight curvature may be noted, the convex side turning towards the violet. On the whole this band behaves exactly like it does in aqueous solution, the only difference being the greater deviation from Beer's law in that case.

In the red, the first strip in A shows transmission to λ 6500, with shading from λ 6050; the seventh strip, transmission to λ 6580, shading from λ 6100. The first strip in B shows transmission to λ 6950, shading perceptibly from λ 6550; while the seventh strip shows transmission as far as λ 7020, with shading from λ 6600. In both sets, therefore, the band narrows slightly with dilution, and in B quite uniformly with the decrease of concentration. In A, however, the narrowing is considerably more rapid at first. Here, again, we find that the band behaves in a manner very similar to what we found in the aqueous solution, only the change is somewhat slower. The decrease in concentration from strip to strip, here, is, however, only about half what it was in the aqueous solution; and taking this into consideration the difference is not as great as it seems at first glance.

Copper Chloride in Ethyl Alcohol—Beer's Law. (See Plate 33.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.744, 0.595, 0.469, 0.372, 0.297, 0.233, and 0.186; the depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. For set B the concentrations were 0.233, 0.186, 0.147, 0.116, 0.093, 0.073, and 0.058; the depths of cell were the same as for set A.

All the solutions were green as seen in their bottles, the color being somewhat more intense than was the case with the methyl alcohol solutions.

The exposures were made only to the Nernst lamp, since it was shown that all the solutions were opaque beyond the visible spectrum. The exposure lasted for 1½ minutes, the width of the slit being as usual 0.01 cm.

We have the same bands as in the methyl alcohol solutions, with the difference that here they are somewhat wider.

The limits of transmission for the first and seventh solutions in A are, respectively, λ 5250 and λ 5080, the edge forming a line which curves slightly from the first to the fourth strips, then becomes straight. The corresponding limits for B are λ 4750 and λ 4600, the edge forming a line which is straight from the first to the fifth solutions, then curves slightly towards the seventh, the convex side being towards the shorter wavelengths. It will be noticed that the edge of the absorption band here is very similar to what we found in the methyl alcohol solutions, the only difference being that here it is located about 400 Ångström units nearer the red end of the spectrum.

The absorption in the red apparently obeys Beer's law quite accurately, the edge of the band remaining in practically the same position for the seven solutions of a set. This position for A is at λ 6200, for B at λ 6700. The shading in A is noticeable at λ 5900, in B at λ 6400. Here, then, the edge of the band is, on the whole, nearer the violet end of the spectrum by about 250 Ångström units than was the case in the methyl alcohol solutions.

COPPER CHLORIDE IN ACETONE—BEER'S LAW. (See Plate 34.)

The concentrations of the solutions used in making the negative for B, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.02, 0.0168, 0.0139, 0.0114, 0.0094, 0.0080, and 0.0066, the corresponding depths of absorbing layer being 8, 9.5, 11.5, 14, 17, 20, and 24 mm. For set A the concentrations were varied from 0.008 to 0.0027, the depths of cell being the same as in B.

The most concentrated solutions were greenish-yellow, from which the color changed gradually to a pale yellow with dilution.

The exposures were made to the light from the Nernst lamp only, a preliminary trial showing that the entire ultra-violet region was absorbed by a comparatively shallow layer of the most dilute solution. The time of exposure was $1\frac{1}{6}$ minutes; the slit having a width of 0.01 cm. as usual.

There is a region of absorption in the violet which in B first narrows slightly with dilution, then begins to widen, and continues to do so throughout the entire range of concentrations studied. The limit of transmission for the most concentrated solution of set A is at λ 4130. In the strip corresponding to the third solution it is at λ 4100, from which it moves regularly towards the red, reaching λ 4150 in the seventh strip.

In the first solution of set A the limit of transmission is at λ 3850. It moves towards the red quite regularly with dilution, reaching λ 3950 in the strip corresponding to the seventh solution. A shows an absorption band having its center at λ 4750. This band, which is about 200 A.U. wide, remains of constant width throughout. In A, though still visible, it is rather faint. Its position is, however, exactly the same as in B.

In the red, both B and A show transmission as far as λ 7400, or to the limit of the sensibility of the plates used. The slight shading in B, however, indicates some absorption in the extreme red, and also points to the conclusion that *this absorption increases somewhat with dilution.*

This is the first case we have found where the absorption increases with dilution when the product of concentration and depth of absorbing layer remains constant, and hence deserves careful consideration. Jones and Uhler found that they could not use solutions of copper bromide in acetone, on account of the chemical action which takes place when the two substances are brought together. It is barely possible that some slight chemical change was taking place in these solutions of copper chloride in acetone, which might not have been sufficient to produce any precipitation, and which might yet have increased with dilution in such a way as to produce the effect observed in the absorption spectrum. The only other case found in this work where this kind of a deviation from Beer's law was observed was that of ferric chloride in acetone, and here the chemical action was very noticeable indeed, the color of the solution deepening very markedly in the course of a few hours. There is hence a reasonable doubt that the effect here observed is real, and until this is decided it is better not to draw any conclusions from the spectrogram just considered.

Copper Chloride in Methyl Alcohol with Water. (See Plate 35.)

The concentration of the copper salt was constant throughout, and equal to 0.15 normal. The percentages of water in the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0, 4, 8, 12, 16, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, and 40. The common depth of absorbing layer was 2.0 cm. The exposures to the light of the Nernst lamp and spark lasted 1 and 3 minutes, respectively, the width of the slit being 0.01 cm.

In the first solution transmission in the blue ceases at λ 4500. From this the limit of transmission moves towards the shorter wave-lengths, fairly regularly with increase in the percentage of water in the solution. It will be noticed that the increments in the percentages of water were 4 per cent from the first to the sixth solutions, whence they were 2 per cent to the end of the series. The absorption in the region of short wave-lengths also recedes more rapidly from the first to the sixth strips, then more slowly, but with perfect regularity, until the last strip is reached, where the limit of transmission is λ 3750. The line formed by the edge of the absorption band in the first six strips is curved somewhat, the concave side facing the region of short wave-lengths. This is what we have always found with the more concentrated solutions of copper chloride. From the sixth to the sixteenth strips the line is nearly straight, the curvature, if any, being in the opposite direction to what it is for the first six strips. In the red the absorption band behaves in an unusual manner, as may be seen from the plate, but which is more easily made out from the negatives, of which the following is a description.

The strip corresponding to the solution containing no water shows complete absorption of all wave-lengths longer than λ 6500. The absorption is very weak at λ 6100, and quite weak even at λ 6300, the absorption band accordingly showing a fairly well-defined edge in the neighborhood of λ 6400. With addition of water up to 12 per cent the absorption increases markedly, the limit of transmission for the fourth strip still being at λ 6500, but the shading has increased very much, the absorption being now as great at λ 6100 as it was at λ 6300 in the first solution. Some absorption is evident as far down as λ 6000. From the fourth to the sixteenth solutions, the percentage of water increased from 12 to 40 per cent, the absorption diminishing slightly; the limit of transmission in the sixteenth solution is at λ 6650. The shading, although still noticeable as far down as λ 6000, is much weaker than in the fourth solution. The point to be specially noted is that the greatest change takes place at first, with addition of water, the change in the total amount of absorption being greater from the first to the second solution than from the second to the third, and so on. The effect of the water may then be said to be twofold. First, it tends to make the edge of the band much more hazy, and secondly, as more of it is added, it tends to narrow up the band somewhat.

Copper Chloride in Ethyl Alcohol with Water. (See Plate 36.)

The concentration of copper chloride was constant throughout and equal to 0.10 normal. The percentages of water in the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0, 4, 8, 12, 16, 20, 24, 28, 32, 36, 40, 44, 48, 52, 56, and 60, the strips being all the same and equal to 4 per cent.

With addition of water, the color of the solutions as seen in the bottles changed from an olive-green to a light-blue. The common depth of cell was 2.0 cm. Exposures to the light of the Nernst lamp and spark lasted, respectively, 1 and 3 minutes, the slit having the usual width of 0.01 cm.

The limit of transmission in the blue and violet region moves towards shorter wave-lengths with addition of water, more rapidly at first, then more and more slowly as the percentage of water is increased, giving the edge of the band a curved form, the convex side being towards the region of shorter wave-lengths. The limit of transmission for the solution containing no water is λ 4800, and for the one containing 60 per cent of water it is at λ 3400. The solution containing 40 per cent of water ceases to transmit at λ 3570, whereas for the methyl alcohol solution containing 40 per cent of water it is at λ 3750. When we consider that the limit of transmission for the solution in pure ethyl alcohol is λ 4800, while for that in pure methyl alcohol it is at λ 4500, we see how much more rapidly the absorption of the ethyl alcohol solution decreases with addition of water. The difference is no doubt to be accounted for by the smaller concentration of the metallic salt in the case now under discussion, the change in the absorption apparently being determined by the ratio of the amount of water to the amount of dissolved salt, rather than by the actual percentage of water in the solvent.

In the red the absorption decreases regularly with addition of water. The limit of transmission for the first solution is at λ 6400, the shading extending to λ 6000. For the sixteenth solution the absorption is complete at λ 6900, shading extending down to about λ 6400. No trace of the effect observed in the case of methyl alcohol solutions was found.

Copper Chloride in Acetone with Water. (See Plate 37.)

The concentration of the copper salt was constant throughout and equal to 0.014 normal. The percentages of water in the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0, 1, 2, 3, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 26, and 30. The depth of cell throughout was 2.0 cm.

The exposures to the light of the Nernst lamp and spark lasted 1⅓ and 3 minutes, respectively, the slight increase in the length of exposure to the Nernst lamp being occasioned by the fact that the line voltage had dropped so low that it was no longer possible to keep the current through the lamp at the usual value of 0.8 ampere. It was accordingly kept at 0.76 ampere, and the time of exposure lengthened as indicated. Before any more work was done, the line voltage was permanently raised by an adjustment of the step-down transformers, so that the current could always be kept at 0.8 ampere.

The solution in pure acetone absorbed completely all wave-lengths shorter than λ 5250. As the percentage of water was increased the absorption moved rapidly towards the violet at first, then more slowly, becoming almost stationary towards the last. The second, third, and fourth strips show the presence of the absorption band at λ 4730. This, however, disappears very rapidly with addition of water. The limit of transmission for the fifth solution, containing 4 per cent of water, is at λ 4500, while for the sixteenth, with 30 per cent of water, it is at λ 4350.

In the red the absorption is slight. The solution in pure acetone, however, shows considerable general absorption throughout the entire red region, and also indicates the presence of a band beyond λ 7000. This band narrows with increase in the percentage of water, no sign of it being visible in the strip corresponding to the seventh solution.

Copper Bromide in Water—Beer's Law. (See Plate 38.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 1.08, 0.72, 0.50, 0.36, and 0.27, the corresponding depths of absorbing layer being 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.18, 0.12, 0.083, 0.06, and 0.045, the depths of cell being the same as for A. The concentration of the mother-solution of copper bromide was 2.16, but its color was so deep-brown, and there was such an amount of general absorption throughout the spectrum, that it was impossible to get any light of sufficient intensity to affect a photographic plate through a layer of it having a depth of 3 mm. Even when diluted to 1.62 normal a layer of 4 mm. in thickness absorbed practically everything except a limited region in the orange-red. The solution whose concentration was 1.08 had a dark olive-green color, the change in color from 1.6 to 1.08 normal being very rapid and striking. With decrease in concentration below 1.08 the color changed gradually to a light-blue.

The exposures to the light of the Nernst lamp and spark lasted, respectively, 1½ and 3 minutes, the slit having the usual width of 0.01 cm.

The bands in the ultra-violet and red both narrow considerably with decrease in concentration, the narrowing being very much greater for the band of shorter wave-lengths. The most concentrated solution in A absorbed everything of shorter wave-length than λ 4550, while the most dilute solution transmitted as far down as λ 3900. For B the corresponding limits are λ 3400 and λ 3120. The line formed by the limits of transmission is visibly curved, the convex side turning towards the region of short wave-lengths. In the red, the limit of transmission for the most concentrated solution of set A is at λ 6400, and for the most dilute at λ 6550. For B the corresponding figures are λ 7250 and λ 7330.

Copper Bromide in Water—Molecules Constant. (See Plate 39 A.)

The concentrations of the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 1.50, 1.22, 0.91, 0.68, 0.52, 0.415, and 0.335; the depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm., respectively.

No data giving the dissociation of copper bromide were at hand, and hence it was assumed to be the same as that of copper chloride. This assumption is perhaps not absolutely correct, but the change in dissociation with change in concentration is undoubtedly so nearly the same that the conditions of "molecules constant" were fulfilled in the series as given to a very high degree of accuracy.

The concentrations and depths of cell are exactly the same as those used in making B of Plate 31; hence the two spectrograms serve well for comparing the absorbing powers of copper chloride and copper bromide.

The limits of transmission for the first and seventh solutions in the region of shorter wave-lengths are λ 5400 and λ 3990, respectively, those in the red being λ 6550 and λ 6400. It appears, therefore, that the bromide absorbs more strongly in the violet than does the chloride, while the two have about the same absorbing power in the red. It might be argued that since the copper bromide molecule is heavier than that of copper chloride, we should expect both absorption bands of the former to be shifted towards the red; and that taking this shift into account the result would indicate a greater absorbing power for the bromide throughout. If this were so, then we should expect that, with decrease in concentration, the absorption bands of the bromide would move towards the violet, as referred to the same bands for the chloride. The reason for this is that with decrease in concentration the salts become more and more strongly dissociated, and, hence, in dilute solutions the spectra ought to resemble each other more and more closely. Now, the violet edge of the region of transmission moves towards shorter wave-lengths by about the same amounts for the two salts, when the changes in concentrations are the same. The red band seems to move a little more towards the violet in the bromide than in the chloride, from the measurements given; but on superimposing the two negatives the two seemed identical, except for the strip corresponding to the most concentrated bromide solution, which shows more absorption, due to the large amount of general absorption of this solution. As stated before, measurements on the limits of transmission in the case of absorption bands, having such hazy edges as the one we are dealing with here, are liable to very considerable errors.

Copper Bromide in Methyl Alcohol—Beer's Law. (See Plate 40.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.089, 0.071, 0.056, 0.045, 0.036, 0.028, and 0.022, the corresponding depths of absorbing layer being 6, 7.5, 9.5, 12, 15, 19, and 24 mm. For B the concentrations were 0.028, 0.022, 0.018, 0.014, 0.011, 0.009, and 0.007; the depths of cell were the same as for A.

The more concentrated solutions were reddish-brown, from which the color changed on dilution to a pale greenish-yellow.

The exposure to the light of the Nernst lamp was 1⅙ minutes with a width of slit of 0.015 cm. for A, and 50 seconds with a slit width of 0.012 cm. for B. No exposures to the light from the spark were made, as a preliminary test showed that even the most dilute solution was opaque in the ultra-violet.

In the region of short wave-lengths, the limits of transmission, corresponding to the most concentrated and most dilute solutions of A, are λ 4800 and λ 4550, while for B the corresponding limits are at λ 4320 and λ 4170, respectively. The line formed by the edge of the absorption band is very nearly a straight line in both cases.

In the red the absorption is slight. The limits of transmission for the most concentrated and most dilute solutions of A are λ 7150 and λ 7200, respectively. In B the edge of the band is sensibly straight, and at right angles to the length of the spectrum strips, its limit being at λ 7350. This is, however, so near the limit of sensibility of the plates used that there was, perhaps, transmission to some little distance beyond this. Comparing this spectrogram with that of copper chloride in methyl alcohol (Plate 32), it is seen that the ultra-violet absorption in the two cases is nearly identical, notwithstanding the fact that the concentration of the chloride was about nine times as great as that of the bromide. This shows at once the great power of the bromide for absorbing light of short wave-lengths, when dissolved in methyl alcohol. The absorption for red light is perhaps not very different for the two salts. A comparison is not possible, owing to the great difference in concentration.

Copper Bromide in Ethyl Alcohol—Beer's Law. (See Plate 41.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.0447, 0.036, 0.028, 0.022, 0.018, 0.014, and 0.011; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. For B the concentrations were 0.014, 0.011, 0.0088, 0.0070, 0.0056, 0.0044, and 0.0035; the depths of cell were the same as in A.

The more concentrated solutions were deep brownish-red, opaque in layers of any considerable depth, from which the color changed on dilution to a light clear-yellow.

The exposures to the light of the Nernst lamp were 1½ minutes with a slit 0.02 cm. wide for A, and 50 seconds with a slit 0.012 cm. wide for B. No exposure to the light of the spark was made, since all the solutions were opaque in the ultra-violet.

Towards the ultra-violet the first solution of A transmitted faintly as far as λ 5500; the seventh solution as far as λ 5050. The corresponding limits for B are λ 4500 and λ 4300, respectively. The edge of the band in either case forms very approximately a straight line. In the red the absorption is very slight, the limit of transmission as shown by A being at λ 7200 and λ 7250, respectively, for the most concentrated and most dilute solution. The solutions of B transmitted perfectly to beyond λ 7400; hence no absorption is registered on the photographic plate.

Compared with the solutions in methyl alcohol, these solutions of copper bromide in ethyl alcohol show very much stronger absorption in the region of shorter wave-lengths. In the red the absorption in the two solvents is not very different, if the differences in concentration are taken into account in making the comparison.

COPPER BROMIDE IN METHYL ALCOHOL WITH WATER. (See Plate 42.)

The concentration of the copper salt was constant throughout, and equal to 0.05 normal. The percentages of water in the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0, 4, 8, 10, 12, 14, 16, 18, 20, 24, 28, 32, 36, 40, 44, and 50. The depth of the absorbing layer was constant and equal to 2.0 cm.

The solution containing no water was brown, and practically opaque in deep layers. With addition of water the color changed rapidly to yellowish-green, and finally became bluish-green in the solutions containing the greatest amount of water.

The time of exposure to the light of the Nernst lamp and spark was, respectively, 1½ and 3 minutes, the slit having, as usual, a width of 0.01 cm.

The limits of transmission for the first eight solutions, beginning with the one containing no water, were λ 5450, λ 4900, λ 4625, λ 4520, λ 4450, λ 4330, λ 4270, and λ 4220. Leaving out the first two, where there was considerable general absorption, the limits fall almost exactly on a straight line. The solution containing 50 per cent of water transmitted as far down as λ 3700.

In the red the absorption band also narrows and quite regularly with addition of water, the bromide behaving in this respect quite differently from the chloride. The extreme limit of transmission for the solution containing no water was λ 6850, there being considerable absorption from λ 6600 on. For the solution containing the largest percentage of water the limit was λ 7250, with considerable shading from λ 6650 on. The edge of the band hence becomes more hazy with addition of water here also, as it did in the case of the chloride.

A comparison of this spectrogram with the one of the chloride in methyl alcohol (Plate 35) shows not only that the absorption of the bromide in the ultra-violet is stronger, but also that it decreases much more rapidly on addition of water. This is undoubtedly due to the much smaller concentration of the bromide, which would make the ratio of water to colored salt very much greater than it was for the chloride. In the red the absorption is about what we should expect from the concentration of the solutions.

COPPER BROMIDE IN ETHYL ALCOHOL WITH WATER. (See Plate 43.)

The concentration of the copper bromide was constant throughout, and equal to 0.06 normal. The percentages of water in the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 30, 35, and 40. The depth of the absorbing layer was in this case only 0.4 cm., owing to the practical opacity of the solutions containing the least amount of water in layers of 2.0 cm. or more.

The first six solutions changed from a deep-brown to a greenish-brown. From the seventh to the sixteenth the color changed from a clear bluish-green to a light greenish-blue. The exposures to the light of the Nernst lamp and spark were, respectively, 1½ and 3 minutes in length; the width of the slit was 0.01 cm.

Leaving out the first two solutions, where the general absorption was so great that very little light was transmitted, we find for the limit of transmission towards the ultra-violet for the third solution λ 4750. From this the limit moves gradually to the shorter wave-lengths, reaching λ 3450 in the solution containing the greatest amount of water. The absorption band here narrows much more rapidly with addition of water than was the case with the solutions in methyl alcohol. A part of this effect is no doubt due to the shallower layer of the solutions here used, but that will hardly account for all of it, since the edge of the band is comparatively sharp, showing that it does not widen very rapidly with increase in the depth of the solution. It can not be accounted for by a difference in concentration, as could be done in the case of the chloride solutions, for here the actual concentration of the ethyl alcohol solutions was greater than that of the solutions in methyl alcohol. The effect is, hence, very probably due to some action of the non-aqueous solvent, or possibly to some mutual action of the water and the non-aqueous solvent, which would be different for the two alcohols.

In the red the band narrows gradually with addition of water, its limit in the solution containing no water being at λ 7100, and reaching the limit of the sensibility of the photographic plates used in the solution containing 18 per cent of water. The smaller amount of absorption here as compared with the methyl-alcohol solutions is to be ascribed to the shallower layer used.

COPPER NITRATE IN WATER—BEER'S LAW. (See Plate 44.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 4.04, 3.00, 2.00, 1.33, 0.92, 0.67, and 0.50; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.67, 0.51, 0.34, 0.22, 0.15, 0.11, and 0.084; the depths of cell were the same as in A.

The most concentrated solutions were blue, and on dilution the color changed to a light greenish-blue. The exposures to the light of the Nernst lamp and spark were of 1 and 3 minutes duration, respectively; the width of the slit being as usual 0.01 cm.

There is an absorption band in the ultra-violet distinct from the NO_3 band which we have seen before. The limit of transmission for the most concentrated solution in A is at λ 3600, from which it moves gradually towards the region of shorter wave-lengths until the fifth solution is reached, where transmission ceases at λ 3390. This is perhaps the limit of the NO_3 band, or very nearly so for solutions of the concentration here used, since there is little or no narrowing of the absorption in passing from the fifth to the seventh strips of A. In B the transmission is sharply limited by the NO_3 band throughout, transmission ceasing at λ 3280.

It is interesting to compare the absorption of this salt with that of copper chloride. The latter in concentrated solutions absorbs not only the ultra-violet, but also all of the violet and blue. It must be evident, then, that all the absorption in the blue, violet, and perhaps also the ultra-violet, in solutions of the chloride and bromide, is to be ascribed to the molecule, or to the molecule and whatever may be associated with it, and not in any way to the ions. The copper ions very likely exert no absorption on light of such short wave-lengths as come within the range of the present investigation.

In the red the most concentrated solution of A absorbs everything of wave-length longer than λ 5980, the most dilute solution of A transmitting some light as far out as λ 6250. For B the limits of transmission for the most concentrated and most dilute solutions are, respectively, λ 7200 and λ 7250, there being considerable shading from about λ 6600 in both cases.

Again comparing the absorption of the nitrate and the chloride, making due allowances for differences in concentration, we find that the red band is sensibly the same for the two salts—emphasizing again the fact that the absorption of red is chiefly a function of the concentration of copper atoms, depending only to a slight extent on their immediate surroundings.

COPPER NITRATE IN WATER—MOLECULES CONSTANT. (See Plate 45.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 4.04, 3.18, 2.36, 1.78, 1.38, 1.11, and 0.92; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm., respectively. The concentrations for B were 1.00, 0.81, 0.60, 0.46, 0.347, 0.273, and 0.223; the depths of absorbing layer were the same as in A. The exposures to the light of the Nernst lamp and spark lasted for 1 and 3 minutes, respectively, the slit being adjusted to a width of 0.01 cm.

A shows that the absorption in the ultra-violet still narrows with dilution, the limits of transmission for the most concentrated and most dilute solutions being, respectively, λ 3600 and λ 3430. In B the transmission is limited by the NO_3 band, the edge of which falls at λ 3280 throughout. Since the ultra-violet absorption narrows even in this, it is evident that something in addition to the simple theory of dissociation is needed to account for the facts.

In the red we find that the band first narrows until the third strip of A is reached, then widens continuously with dilution, the edge forming a curved line concave towards the violet. The limit of transmission for the first solution is λ 6000, for the third λ 6050, and for the seventh it is at λ 5950. In B the absorption increases regularly with dilution, the limit in the first solution being at λ 6800 and at λ 6650 for the seventh. There is considerable shading, but this also increases somewhat with decrease in concentration.

In general, the absorption spectrum of copper salts in the region of the spectrum investigated is much simpler than that of cobalt salts, inasmuch as it presents only two or at most three absorption bands. Of these, only the one at λ 4730 in acetone solutions lies wholly in the spectral region studied; the band in the ultra-violet is what might be termed one-sided, no region of transparency on its more refrangible side having ever been found. The band in the red is, however, strictly a band, a region of transparency existing in the infra-red. The behavior of this band throughout strongly suggests the green band of cobalt salts in solution, while the ultra-violet absorption is somewhat different from anything we have found thus far, resembling more nearly the absorption of iron salts, to be discussed in the next chapter.

Since the absorption in the ultra-violet decreases rapidly with dilution, when the product of concentration and depth of layer is kept constant, it seems reasonable to suppose that the copper ion has little or nothing to do with it, and hence that it must be ascribed to the molecules; but as the absorption decreases with dilution, even when molecules are kept constant, without, however, entirely disappearing (as was the case with some cobalt bands), we must conclude that the absorbing power of a molecule is influenced considerably by its immediate surroundings. As usual, there are at least two possible ways of explaining the increase in the absorption with concentration, when molecules are kept constant. One is to assume the formation of aggregates of molecules, and that the absorbing power of the molecule is increased thereby; the other is to assume the existence of solvates, and that the absorbing power of a molecule decreases with increase in the complexity of the solvate. To decide between these two possible explanations we need only take into account the change in the absorption produced by a rise in the temperature of the solution. This change is the same qualitatively as that produced by increasing the concentration. Molecular aggregates are broken down by rise in temperature, and hence, by the assumption made above as to the effect of aggregates on absorption, this should *decrease* the absorption instead of *increasing* it. We must conclude, therefore, that the change in the absorption is not due to the formation of aggregates.

Solvates are made simpler both by increasing concentration and by rise in temperature; and, accordingly, from the assumption stated above regarding the effect of complexity of solvates on absorption, both changes should produce similar differences in the absorption spectrum, which is in accordance with observed facts. We conclude, therefore, that the ultra-violet absorption of solutions of copper salts is due to the "solvated" molecules of the dissolved salt, and that the absorbing power of such molecules is decreased as the complexity of the solvate increases.

It will be remembered that for equal concentrations the absorption in the region of shorter wave-lengths is least in the aqueous solutions, then increases as we pass from methyl alcohol to ethyl alcohol. In general, also, it may be stated that the change in the absorption with dilution is greatest for the aqueous solution, and then decreases as we pass to methyl and ethyl alcohols. This is just what we should expect, since the power to form solvates is greater with water than with either of the alcohols, and greater for methyl than for ethyl alcohol; hence, in solutions of equal concentration the solvates should decrease in complexity when we pass in the direction—water, methyl alcohol, ethyl alcohol. Also, on dilution, the change in the complexity of the solvate should be greater in the water solutions than in the methyl or ethyl alcohol solutions.

The absorption band in the red narrows somewhat when the product of concentration and depth of absorbing layer is kept constant, but widens when molecules are kept constant. Its intensity does not change nearly as much when the solvent is changed as was the case with the violet band, the concentration being the chief factor determining it. We hence conclude that this band, like the green band of cobalt salts, is due to the metallic atom, and that its absorbing power is affected only slightly by its immediate surroundings. The peculiar behavior of the red band of copper chloride in methyl alcohol, on addition of water, is interesting, especially as its explanation is not at all difficult, although it may not at first seem so simple. It will be recalled that here the band first widened when water was added, and then, as the amount of water was increased, it narrowed regularly. Now, when a small amount of water is added it is reasonable to conclude that the hydrates formed would be comparatively simple, and that as the amount of water is increased their complexity also increases.

We have stated that the effect of the surroundings on the absorption of the copper atom for this region of the spectrum is slight compared with what it is in the ultra-violet; but that it is quite appreciable is shown by the narrowing of the band wherever the conditions for Beer's law hold. We believe that this narrowing is due to a change in the complexity of the solvates. To explain the case in question, then, we need only say that the absorption of the comparatively simple hydrates formed when a small amount of water is added is greater than that of the methyl alcoholates already existing in the original solution; and that, therefore, the first effect observed is a widening of the band. Its subsequent narrowing as more water is added is, of course, due to the increase in the complexity of the hydrates.

In the similar solutions in ethyl alcohol the band narrowed from the very first, which is just what we should expect, since the solvates here are simpler than in methyl alcohol and hence their absorbing power would be equal to or greater than that of the simple hydrates first formed.

CHAPTER V.

SALTS OF IRON.

FERRIC CHLORIDE IN WATER—BEER'S LAW. (See Plates 46 and 47 B.)

The concentrations of the solutions used in making the negative for A, Plate 46, beginning with the one whose spectrum is adjacent to the numbered scale, were 1.30, 0.97, 0.65, 0.43, 0.30, 0.22, and 0.16; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B, Plate 46, the concentrations were 0.22, 0.16, 0.11, 0.073, 0.051, 0.037, and 0.027; and for B, Plate 47, 0.037, 0.028, 0.018, 0.012, 0.0085, 0.0062, and 0.0048; the depths of cell in both cases were the same as for A, Plate 46.

The most concentrated solutions were reddish-orange as viewed in their bottles, from which the color changed through orange-yellow to nearly colorless in the last members of the third series. The exposure to the light of the Nernst lamp lasted for 1 minute, the slit having a width of 0.01 cm. No exposure to the light from the spark was made, as it was ascertained by a preliminary trial that even the most dilute solution was opaque in the entire ultra-violet beyond λ 3600. A trial also showed complete transmission in the red as far as λ 7400, and hence no red-sensitive plates were used. Hence, all the spectra of iron salts shown in this chapter seem to end at λ 6000 or near there, which simply shows that the Seed film used was not sensitive to light of wave-length longer than about λ 6000.

The absorption decreases fairly regularly with dilution, the decrease being, however, less at high dilutions. The limits of transmission for the most concentrated and most dilute solutions of each of the three sets are, respectively, λ 4850 to λ 4600, λ 4220 to λ 4100, and λ 3900 to λ 3800, showing that whereas the narrowing of the band in the first set amounted to 250 A.U., in the third set it was only 100 A.U.

An attempt was made to carry the dilution still farther, but it was found that the very dilute solutions changed color so rapidly with time that it was impossible to use them and place confidence in the results.

FERRIC CHLORIDE IN WATER—MOLECULES CONSTANT. (See Plate 48.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 1.30, 1.00, 0.75, 0.53, 0.40, 0.30, and 0.22, the corresponding depths of absorbing layer being 3, 4, 6, 9, 13, 18, and 24 mm. For B, the concentrations were 0.25, 0.20, 0.135, 0.10, 0.07, 0.05, and 0.04; the depths of cell were the same as for A.

The exposures were of 1 minute duration, and were made to the light of the Nernst lamp only.

It will be seen that even here the absorption decreases somewhat with dilution, the narrowing of the band in A amounting to 140 A.U., and in B to about 100 units.

Ferric Chloride with Calcium Chloride. (See Plates 49 and 51 A.)

The concentration of ferric chloride in the solutions used in making the negative for A, Plate 49, was constant and equal to 0.182 normal. The concentrations of calcium chloride, beginning with the solution whose spectrum is adjacent to the scale, were 3.97, 3.40, 2.85, 2.30, 1.75, 1.20, 0.64, and 0.00. For B the concentration of ferric chloride was 0.035, and for A, Plate 51, it was 0.007; the concentrations of the calcium salt were the same as for A, Plate 49. The common depth of absorbing layer was 1.5 cm.

The dilute solutions without calcium chloride were yellow, or very faint yellow, depending upon concentration. With increasing amount of the calcium salt the color deepened very markedly, becoming orange to reddish-orange, according to the concentration of the colored salt.

The spectrograms show the marked increase in width of the absorption band with addition of the dehydrating agent. In A the solution containing no calcium chloride transmits as far as λ 4600, while the one containing the greatest amount of the calcium salt ceases to transmit at λ 5250. For B the corresponding wave-lengths are λ 4150 and λ 4950, and for A, Plate 51, they are λ 3860 and λ 4620, respectively.

In each case the line formed by the limits of transmission is curved, with its concave side towards the region of short wave-lengths, showing that the absorption decreases most rapidly at first with addition of the calcium salt. The increments in the concentration of the dehydrating agent from solution to solution were sensibly the same, namely 0.55 normal.

Ferric Chloride with Aluminium Chloride. (See Plates 50 and 51 B.)

The concentration of the iron salt in the solutions used in making the negative for A, Plate 50, was constant and equal to 0.182 normal. The concentrations of aluminium chloride, beginning with the solution whose spectrum is adjacent to the numbered scale, were 2.61, 2.25, 1.88, 1.52, 1.16, 0.79, 0.43, and 0.00; the successive increments in concentration were all 0.366, except the last, which is 0.43. For B the concentration of ferric chloride was 0.035, and for B, Plate 51, it was 0.007, the concentrations of the aluminium chloride being the same as for A, Plate 50.

The common depth of absorbing layer was 1.5 cm., and the exposure which was made to the light of the Nernst lamp lasted only 1 minute, the slit having the usual width of 0.01 cm.

The spectrograms are very similar to those made with the solutions containing calcium chloride as dehydrating agent, the only difference being the somewhat greater widening of the absorption band in the present case. Since the concentrations of the iron salt were the same, set for set, with calcium chloride, as in the present case, the spectrograms are directly comparable.

The limits of transmission for the solutions containing no dehydrating agent are of course the same in the two cases, as we need only compare the limits for the solutions containing the greatest amount of the calcium or aluminium salt. We find that in the series containing the greatest amount of the iron salt, the limit of transmission is 50 A.U. nearer the red end of the spectrum for the solution containing the aluminium salt than for the one containing the calcium salt. For the solution containing ferric chloride, at concentration 0.035, the difference is again 50 A.U., while for the one having the concentration 0.007 the difference amounts to 80 units.

FERRIC CHLORIDE IN METHYL ALCOHOL—BEER'S LAW. (See Plates 52 and 54 A.)

The concentrations of the solutions used in making the negative for A, Plate 52, beginning with the one whose spectrum is adjacent to the numbered scale, were 1.23, 0.923, 0.615, 0.410, 0.284, 0.205, and 0.135; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B, Plate 52, the concentrations were 0.2, 0.15, 0.1, 0.066, 0.046, 0.034, and 0.025, and for A, Plate 54, they were 0.034, 0.026, 0.017, 0.011, 0.0078, 0.0057, and 0.0042; the depths of cell were the same as in A, Plate 52.

The most concentrated solutions were deep orange-red, from which on dilution the color changed to a clear yellow.

The exposure which was made to the Nernst lamp lasted only 1 minute, the slit having the usual width of 0.01 cm. No exposure was made for the red end of the spectrum, as examination by the direct-vision spectroscope showed no absorption in this region.

The three spectrograms show that Beer's law holds very accurately over the range of concentrations studied, the edge of the absorption band remaining unchanged in position in any one series. In A, Plate 52, the limit of transmission is at λ 5300, in B at λ 4950, and in A, Plate 54, it falls at λ 4600.

In A, Plate 46, the limit of transmission was not far from λ 4700. The concentrations and depths of cell there were about the same as in A, Plate 52, while the solvent there was water and here methyl alcohol. This indicates considerably greater absorbing power for the salt when dissolved in methyl alcohol, if, as is usual, the actual shift of the center of the absorption band is not very great. In the present case, since Beer's law holds, we may assume that all the moving parts containing an iron atom are equally active in absorbing light; while in the aqueous solution, since Beer's law does not hold, some of them must either not absorb at all, or else much more feebly than others.

FERRIC CHLORIDE IN ETHYL ALCOHOL—BEER'S LAW. (See Plates 53 and 54 B.)

The concentrations of the solutions used in making the negative for A, Plate 53, beginning with the one whose spectrum is adjacent to the numbered scale, were 1.23, 0.923, 0.62, 0.41, 0.28, 0.21, and 0.15; the corresponding depths of cell being 3, 4, 6, 9, 13, 18, and 24 mm. For B, Plate 53, the concentrations were 0.20, 0.15, 0.10, 0.066, 0.046, 0.034, and 0.025; and for B, Plate 54, 0.034, 0.026, 0.017, 0.011, 0.0078, 0.0057, and 0.0042; the depths of absorbing layer were the same as in A, Plate 53.

The color of these solutions was identical with that of the solutions in methyl alcohol. The exposure, which was made to the light of the Nernst lamp, lasted only for 1 minute; the slit had a width of 0.01 cm.

It will be seen that here also Beer's law holds fairly well, the deviation from it in the most concentrated series causing the band to narrow by something like only 40 A.U. In the intermediate series the narrowing of the band with dilution is still less, only about 25 or 30 A.U., and so may very probably be due to a gradual shift in the position of the film during the exposure. In the most dilute series no change in the width of the region of absorption can be noted. The slight deviation observed in the first series may perhaps be due to mutual influence of the absorbers, as pointed out in the introductory chapter.

Comparing these spectrograms with those of solutions in methyl alcohol, we find that the limit of transmission here is always a little nearer the region of short wave-lengths, which is a little different from what we have usually found. The rule has been that the absorbing power of any substance in ethyl alcohol is somewhat greater than in methyl alcohol, while here the opposite is true. Ferric chloride is, however, a rather unstable substance in solution, and it is possible that the anomalies which we have noted are due to some chemical change which has not been taken into account.

FERRIC CHLORIDE IN ACETONE—BEER'S LAW. (See Plate 55.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.086, 0.064, 0.043, 0.029, 0.020, 0.014, and 0.011; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.014, 0.010, 0.007, 0.0047, 0.0032, 0.0023, and 0.0017, the depths of cell being the same as for A.

The most concentrated solutions were red, from which on dilution the color changed to yellow. The exposure, which was made only to the light from the Nernst lamp, lasted 1 minute, the slit having the usual width of 0.01 cm.

It was observed that a solution of ferric chloride in acetone, on being allowed to stand, changes color slowly with time, the color becoming deeper. A solution which when freshly made up was yellow, was found to be a clear orange after two days. In order to obtain the spectra photograph before any appreciable change took place, it was necessary to make the exposure just as soon as the solution was made up, and this was done, the time elapsing between making up the series and completing the exposures for the spectrogram being not more than 30 minutes.

The negative for A shows a decrease of absorption with dilution, while B shows no change in the width of the band. This is the same as what we just found in the case of the solutions in ethyl alcohol, only the narrowing of the band in the concentrated solutions is much greater with acetone.

CHAPTER VI.

SALTS OF CHROMIUM.

A comparatively large number of investigators have worked on salts of chromium from the standpoint of absorption of light. We need only mention the work of Talbot,[1] Brewster,[2] Croft,[3] Müller,[4] Gladstone,[5] Melde,[6] the early work of Hartley,[7] Vierordt,[8] Vogel,[9] E. Wiedermann,[10] Soret,[11] Settegast,[12] Moissan,[13] Pulfrich,[14] Zimmermann,[15] Becquerel,[16] Liveing and Dewar,[17] Schunck,[18] Recoura,[19] and Sabatier.[20]

Knoblauch,[21] in his interesting and important investigation on the absorption spectra of very dilute solutions, studied a number of chromium compounds. These were the chloride, nitrate, sulphate, acetate, oxalate, potassium chrom-oxalate, and chrom-alum. Knoblauch directed a part of his work to testing the consequences of the then recently proposed theory of electrolytic dissociation. According to this theory, the absorption spectrum of a concentrated solution must be different from that of a very dilute solution; and at dilutions of complete dissociation, all of the salts of an acid with a colored anion, having colorless cations, or all of the salts of a metal having colorless anions, must have the same absorption spectrum. Knoblauch found that neither of these conclusions from the theory was verified experimentally.

Ostwald[22] showed a little later that the second consequence of the theory is fully verified by experimental facts.

Knoblauch also tested Beer's law, and found that it held for many salts within wide limits of concentration. He concluded that the apparent deviations from the law are to be explained as due to chemical or physical changes in the solutions.

---

[1] Phil. Mag. (3), **4**, 112 (1834).
[2] Phil. Trans., 1835, 1, 91, and Phil. Mag. (4), **24**, 441 (1862).
[3] Ibid. (3), **21**, 197 (1842).
[4] Pogg. Ann., **72**, 76 (1847), and **79**, 344 (1850).
[5] Phil. Mag. (4), **14**, 418 (1857), and Journ. Chem. Soc., **10**, 79 (1858).
[6] Pogg. Ann., **124**, 91 (1865).
[7] Proc. Roy. Soc., **21**, 499 (1873).
[8] Ber. d. deutsch. chem. Gesell., **5**, 34 (1872).
[9] Ibid., **11**, 913, 1363 (1878).
[10] Wied. Ann., **5**, 500 (1878).
[11] Arch. Sci. Phys. et Nat. (2), **61**, 322 (1878); (2), **63**, 89 (1878).
[12] Wied. Ann., **7**, 242 (1879).
[13] Compt. rend., **93**, 1079 (1881).
[14] Ztschr. f. Kryst., **6**, 142 (1882).
[15] Lieb. Ann., **213**, 285 (1882).
[16] Ann. Chim. Phys. (5), **30**, 5 (1883).
[17] Proc. Roy. Soc., **35**, 71 (1883).
[18] Chem. News, **51**, 152 (1885).
[19] Compt. rend., **102**, 515 (1886), **112**, 1439 (1891).
[20] Ibid., **103**, 49 (1886).
[21] Wied. Ann., **43**, 738 (1891).
[22] Ztschr. phys. Chem., **9**, 579 (1892).

Hartley,[1] in his elaborate investigations on absorption spectra, studied a number of salts of chromium. The salt $Cr(NO_3)_3.9H_2O$ is violet in color. When heated to 100° it changes to green. Hartley concludes that the violet are the normal salts of chromium, while the green are chromyl salts, thus:

	Violet salts.	Green salts.
Chloride	$CrCl_3.3H_2O$	$Cr_2OCl_4.2H_2O$
Sulphate..........	$Cr_2(SO_4)_3.15H_2O$	$Cr_2O(SO_4)_2.XH_2O$
Nitrate	$Cr_2(NO_3)_6.9H_2O$	$Cr_2O(NO_3)_4.H_2O$

An interesting paper by Vernon[2] on "The Dissociation of Electrolytes in Solution as Shown by Colorimetric Determinations," was published in sections in the Chemical News. Chromium plays in this work what might be termed the exceptional rôle, as is seen from the following conclusions drawn by the author :[3]

> Almost all the solutions of the thirty-five colored salts examined show considerable decrease in color effect on dilution, due in all probability to dissociation taking place. The only exceptions are certain chromium derivatives, the color of whose solutions, on gradual dilution, either remains constant or increases slightly. All solutions of salts, with the exception of those of certain chromium derivatives and perhaps of potassium permanganate increase considerably in color effect on being heated.

Lapraik[4] has described a large number of empirical relations between the absorption spectra of compounds of chromium. Certain classes of chromium compounds were found to have the same absorption spectra in solution and in the solid state. The band λ 710 to λ 692 is present in all of the chromium compounds investigated, with the exception of potassium chromium cyanide. In certain compounds, however, the band is displaced somewhat from the above position.

The broad absorption in the green in the region of λ 550 to λ 650 is present in all chromium compounds, sometimes displaced somewhat towards the red, in other compounds towards the blue, as referred to the above wave-lengths.

Etard[5] studied the sulphate of chromium, chrome alum, and violet chromium nitrate. He found a band in the red which was characteristic of chromium salts, and which extended from λ 670 to λ 678. He concluded that the absorption spectra of chromium salts are due to the molecules.

The absorption bands produced by an element are displaced in position, or may cease to exist entirely, depending upon the nature of the whole molecule which is in solution, *i.e.*, upon the particular compound of the element studied.

CHROMIUM CHLORIDE IN WATER—BEER'S LAW. (See Plate 56 A.)

The concentrations of the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.53, 0.40, 0.26, 0.17, 0.12, 0.09, and 0.07; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm.

---

[1] Chem. News, **65**, 15 (1892). Dublin Trans. (2), **7**, 253 (1900).

[2] Chem. News, **66**, 104, 114, 141, and 152 (1892).

[3] Ibid., **66**, 154 (1892).

[4] Journ. prakt. Chem., **47**, 305 (1893).

[5] Compt. rend., **120**, 1057 (1895).

The exposures to the light of the Nernst lamp and spark lasted, respectively, 1⅛ and 3 minutes, the slit having a width of 0.01 cm.

In deep layers the more concentrated solutions were red, while in shallow layers they were green. The dilute solutions appeared green as seen in their bottles.

The spectrogram shows three regions of absorption. One is located in the extreme ultra-violet, cutting off the part of the spectrum lying to the more refrangible side of λ 2840. Another absorption band is in the violet, its more refrangible limit being at λ 3900 and moderately well defined, while the red edge, which is more hazy, is near λ 4450. A third band is located in the yellow and orange. Both edges of this band are very diffuse, the red edge slightly more than the blue. The spectrograms indicate the opposite to be the case, but this is due to the fact that the blue edge of the band falls near the region of minimum sensibility of the Seed film, and hence the shading there is very much accentuated. The limits of transmission are at λ 5650 and about λ 6200, although there is considerable absorption as far "down" as λ 5200 and as far up as λ 6750. From λ 6800 to the end of the visible red the solutions are remarkably transparent, which was made very evident by the fact that a concentrated solution, about 20 cm. in depth, still transmitted red light freely, although not a trace of green could be seen through a layer 5 cm. deep.

The width of all these bands is absolutely unchanged by change in dilution, within the limits of concentration here used, showing that the absorption is strictly proportional to the number of chromium atoms in the path of the beam of light, and independent of whether they exist as ions or combined with other atoms in a molecule.

CHROMIUM CHLORIDE IN WATER—MOLECULES CONSTANT. (See Plate 56 B.)

The concentrations of the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.45, 0.35, 0.245, 0.173, 0.125, 0.093, and 0.074; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. The exposures to the light of the Nernst lamp and spark lasted, respectively, 1⅛ and 3 minutes; the width of the slit was 0.01 cm.

The spectrogram shows the same regions of absorption as A, but in this case they all widen with decrease in concentration, as was to be expected. The bands all widen to nearly the same extent. The shading on the red side of the least refrangible band does not extend any farther into the red with decrease in concentration, indicating that this band has a fairly well-defined limit near λ 6800.

A rather narrow band of absorption may be seen at λ 6690. It is faint and scarcely noticeable in A. Its width is not easy to determine, but appears to be only about 30 A.U.

CHROMIUM CHLORIDE WITH CALCIUM CHLORIDE AND ALUMINIUM CHLORIDE. (See Plate 57.)

The concentration of the chromium chloride was constant throughout and equal to 0.074. The concentrations of calcium chloride, beginning with the solution whose spectrum is adjacent to the numbered scale of A, were 3.96, 3.45, 2.85, 2.30, 1.75, 1.20, 0.64, and 0.0. The concentrations of aluminium chloride in the solutions used in making B were, taken in the same order, 2.58, 2.25, 1.86, 1.50, 1.14, 0.78, 0.42, and 0.0.

The common depth of absorbing layer was 1.5 cm., and the times of exposure to the light of the Nernst lamp and spark were, respectively, $1\frac{1}{6}$ and 3 minutes; the slit had the usual width of 0.01 cm.

The effect of adding these dehydrating agents is to widen all the absorption bands, the widening seeming to increase a little more rapidly the more concentrated the solution of the dehydrating agent. This gives the edges of the bands a slightly rounded appearance.

It is also noticed that the effect of the aluminium salt is a little greater than that of the calcium salt, although the concentrations were so chosen as to make the number of chlorine atoms added as nearly the same as possible. The widening can not be due to a driving back of the dissociation of the chromium salt, since we have just seen that the absorption of the chromium chloride does not in any way vary with its dissociation. The most probable explanation here as elsewhere is that some simple hydrates are formed, which normally do not exist except in *very concentrated solutions or at high temperatures,* and that the absorbing power of a chromium atom thus hydrated is greater than when the hydrate is more complex.

The band in the red at λ6690 shows faintly on the negatives for both these spectrograms, although it can not be seen in the reproduction. It does not seem to be affected to any appreciable extent by addition of the foreign salts.

CHROMIUM NITRATE IN WATER—BEER'S LAW. (See Plate 58 A.)

The concentrations of the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.754, 0.564, 0.377, 0.251, 0.174, 0.126, and 0.094; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. The exposures to the light of the Nernst lamp and spark lasted, respectively, $1\frac{1}{6}$ and 3 minutes, the slit having the usual width of 0.01 cm.

The solutions of the nitrate are similar in color to those of the chloride already described, excepting that the latter is relatively more transparent in the green and less so in the red. The result is that in layers of any depth the nitrate solutions are more apt to show red, especially in gaslight. Dilute solutions or very thin layers of concentrated solutions are greenish in color.

The spectrogram shows the same absorption bands as we have already found and discussed for the chloride. Owing to the fact that the concentration of the solutions of the nitrate was somewhat greater, the bands are wider and their edges are much sharper.

In the ultra-violet the transmission is sharply limited by the NO_3 band, and hence we find absorption complete from λ 3270 to the end of the spectrum.

In the most concentrated solution, the violet band begins at λ 3710 and ends at λ 4450, these figures being the limits of (photographic) transmission. Owing to the slight shading the absorption extends somewhat farther to both sides. In the most dilute solutions the limits are λ 3710 and λ 4420, showing a slight narrowing of the band from the red side.

The limits for the yellow band in the most concentrated solution are λ 5170 and λ 6220, while for the most dilute they are λ 5250 and λ 6150, showing considerable narrowing with decrease in concentration.

It will be noticed that both the bands are somewhat nearer the region of shorter wave-lengths in the nitrate than in the chloride, the centers of the two bands for the latter being λ 4175 and λ 5925, while for the former the corresponding figures are λ 4065 and λ 5700. The yellow band in the nitrate is also much hazier on its violet side than was the case with the chloride. This is not brought out by the reproduction, or even by the negative made with the Seed film, on account of the fact that the edge of the band falls so near the middle of the minimum in the sensibility curve of the Seed emulsion. A negative made on a Wratten panchromatic plate, giving both edges of the band, however, shows very clearly the difference in the shading, this being nearly twice as great on the violet side as on the red.

The negative shows the band at λ 6690 rather better than did those made with the chloride solutions. The band is rather faint, but may be seen well enough to enable one to determine its position and general character. It remains of constant width and intensity throughout. Its maximum of intensity falls very close to λ 6690, from which position a gradual shading extends to a distance of about 20 A.U. on both sides. Except for this band, the solutions are almost perfectly transparent from λ 6400 to the end of the visible red.

CHROMIUM NITRATE IN WATER—MOLECULES CONSTANT. (See Plate 58 B.)

The concentrations of the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.70, 0.55, 0.39, 0.28, 0.20, 0.15, and 0.12; the corresponding depths of cell were 3, 4, 6, 9, 13, 18, and 24 mm. The exposures and slit width were the same as used with Plate 58 A.

The spectrogram shows the same bands as Plate 58 A, only here they all widen somewhat with dilution, as was to be expected from their behavior when the conditions for Beer's law were fulfilled.

CHAPTER VII.

SALTS OF NEODYMIUM, PRASEODYMIUM, AND ERBIUM.

Some of the more important investigations on the salts of the above-named elements are the following:

Bahr and Bunsen[1] in their early work on absorption spectra included didymium and erbium.

Becquerel,[2] in his study of spectra in the infra-red region, worked with didymium. In his subsequent work[3] on the variation of absorption spectra in crystals, the sulphate and nitrate of didymium were included.

Becquerel[4] compared the absorption spectra of crystals of didymium salts with the spectra of the aqueous solution of the same salts. He showed that from the displacement of the bands he could recognize distinct substances or definite compounds. He showed that in the crystals we may have, simultaneously, mixtures of different compounds and especially basic salts.

Demarçay[5] studied the spectrum of didymium, and concluded that in addition to praseodymium and neodymium there was probably present a third element. In a subsequent investigation[6] he shows that neodymium from entirely different minerals and sources always has the same spectrum, and concludes that it is a chemical element.

Krüss and Wilson[7] carried out an elaborate investigation on the absorption spectra of the rare earths. They concluded that we must assume the existence of more than twenty elements in the various rare earth minerals.

Bettendorff[8] carried out three investigations on the spectra of the cerium and yttrium group, and Schottländer[9] made use of his spectroscopic studies and spectrophotometric work to characterize the various rare earths.

Boudouard[10] effected the separation of neodymium and praseodymium by means of potassium sulphate instead of ammonium nitrate. The absorption spectra indicated a nearly complete separation from praseodymium.

Scheele[11] did some very careful work on praseodymium in connection with his determination of the atomic weight of that element, and later[12] in connection with the separation of praseodymium and neodymium.

---

[1] Lieb. Ann., **137**, 1 (1886).

[2] Ann. Chim. Phys. (5), **30**, 5 (1883).

[3] Ibid. (6), **14**, 170 (1888).

[4] Ibid. (6), **14**, 257 (1888).

[5] Compt. rend., **102**, 1551 (1886), **105**, 276 (1887).

[6] Ibid., **126**, 1040 (1898).

[7] Ber. d. deutsch. chem. Gesell., **20**, 2134 (1887).

[8] Lieb. Ann., **256**, 159 (1890); **263**, 164 (1891); **270**, 376 (1892).

[9] Ber. d. deutsch. chem. Gesell., **25**, 569 (1892).

[10] Compt. rend., **126**, 900 (1898).

[11] Ztschr. anorg. Chem., **17**, 310 (1898).

[12] Ber. d. deutsch. chem. Gesell., **32**, 409 (1899).

The elaborate investigations of Muthmann[1] and his coworkers, Stützel, Böhm, Baur, Hofer, and Weiss, call for special comment. They raise the question as to the elementary nature of praseodymium and neodymium, and point out certain lines of evidence based on spectrum analysis which make it not impossible that these substances are mixtures. They show that by spectrum analysis it is possible to determine approximately the amounts of neodymium and praseodymium in a mixture of the two, a fact which had earlier been utilized by Jones[2] in his work on the atomic weights of these two elements.

By the electrolysis of fused neodymium compounds Muthmann was able to prepare the pure metal. He then studied the physical properties not only of neodymium, but also of cerium, lanthanum, and praseodymium, which were prepared in the same manner.

An important and interesting investigation was carried out by Liveing[3] on the effects of dilution, temperature, nature of the solvent, etc., on the absorption spectra of solutions of didymium and erbium salts. His eye observations were made with an ordinary spectroscope, and the photographs also with a prism spectroscope. He obtained some very good plates, indeed, considering the kind of apparatus employed. He studied the effect on the absorption of increasing the dilution of the solution, and established the four following facts:

The spectra of the different salts of the same metal in dilute solution are identical. The spectrum is constant for the chloride and sulphate in different dilutions, as long as the thickness of the absorbing solutions is proportional to the dilution. The spectrum of the nitrate is modified by some cause with increasing concentration.

The absorption of the short wave-lengths, which differ for different salts, diminishes with increased dilution.

The effect of rise in temperature from about 20° to 97° renders the bands more diffuse, but does not increase their intensity.

The addition of acid made the absorption in general more diffuse, but did not weaken the absorption.

From this fact, together with the fact that rise in temperature does not increase the intensity of absorption, Liveing concluded that absorption can not be accounted for on the basis of electrolytic dissociation.

The work of Liveing on absorption in non-aqueous solvents is of special interest in the present connection.

He says that didymium chloride dried at a temperature above 100° is quite insoluble in alcohol. This was doubtless due to the formation of the basic chloride. This salt can be heated to 140° to 150° in a current of dry hydrochloric acid gas, and the anhydrous salt is still perfectly soluble in alcohol. The salt with which he worked doubtless contained more or less water.

Liveing says that the absorption spectrum of the alcoholic solution shows the same bands as an aqueous solution, but they are somewhat modified. The positions of maximum absorption are all moved towards the red. The shift of the different bands is not equal. The bands in the yellow and green in the alcoholic solution are so shifted as to suggest the appearance of new bands, but Liveing says that by studying solutions of different concentrations he has convinced himself that no new bands appear. We shall see that this is an error.

---

[1] Ber. d. deutsch. chem. Gesell., **32**, 2653 (1899); **33**, 42, 1748, 2028 (1900); Lieb. Ann., **320**, 231 (1902).

[2] Amer. Chem. Journ., **20**, 345 (1898).

[3] Camb. Phil. Soc., **18**, 298 (1900).

Liveing found the same modifications of the spectrum in aqueous solutions produced by glycerol as by alcohol. Liveing[1] concludes thus:

> On a review of the whole series of observations, I conclude that the characteristic absorptions of didymium compounds, namely those which are common to dilute aqueous solutions, and are only modified by concentration, by heat, and by variations of the solvent, are due to molecules which are identical in all cases, though their vibrations are modified by their relations to other molecules surrounding them.

Urbain[2] devised a new method for separating the rare earths, using ethyl sulphate.

Drossbach,[3] in his work on absorption in the region of the ultra-violet, measured a number of the bands of praseodymium and neodymium; and Hartley,[4] in his work on the absorption spectra of metallic nitrates, included the nitrate of erbium. In discussing his results, Hartley calls attention to the fact that Bunsen[5] found that didymium salts in the crystallized state and in solution show absorption bands that vary in width with the thickness of the absorbing medium and with the quantity of the salt. Solutions of the chloride, sulphate, and acetate, each containing the same weight of didymium, yielded different spectra, the bands being shifted towards the red end of the spectrum with increase in the molecular weight of the salt.

Hartley calls attention to the fact that more recently Becquerel[6] observed similar variation in the absorption spectra, both in crystals and in solutions, while Muthmann and Stützel[7] found marked differences between the spectra of solutions of the different salts of neodymium, such as the chloride, nitrate, and carbonate. As Hartley points out, these facts can not be reconciled with the theory that the absorption spectra of solutions of neodymium salts are due to the neodymium ion, since the solutions of the above-named salts contain, for comparable concentrations, practically the same number of neodymium ions.

Among the more recent investigations made upon the salts of the rare earths is that of Miss Helen Schaeffer.[8] She attempted to test Kundt's law for the nitrates of certain rare earths such as neodymium and cerium. She employed the following solvents: Water, methyl alcohol, ethyl alcohol, propyl alcohol, isobutyl alcohol, amyl alcohol, allyl alcohol, glycerol, and acetone. Solutions were studied containing 1 gram of the salt in

---

[1] Camb. Phil. Soc., **18**, 314 (1900).
[2] Compt. rend., **126**, 835, **127**, 107 (1898).
[3] Ber. d. deutsch. chem. Gesell., **35**, 1486 (1902). Ann. Chim. Phys. (7), **19**, 184 (1900).
[4] Journ. Chem. Soc., **83**, 221 (1903).
[5] Pogg. Ann., **128**, 100 (1866).
[6] Compt. rend., **104**, 777, 1691 (1887).
[7] Ber. d. deutsch. chem. Gesell., **32**, 2653 (1899).
[8] Phys. Ztschr., **7**, 822 (1906).

10 c.c. of the solvent. She found that, in general, the bands had a different arrangement in the various solvents; and in order to identify the bands, she worked with mixtures of the various solvents, so as to get what she supposed was a gradual shift of the bands. Her plates, however, show that instead of having a shift in the bands, she had two sets of bands existing simultaneously.

In the second part of her investigation she studied change in absorption with change in concentration; in other words, Beer's law. She found that with decreasing concentration there is a shift of the yellow band towards the violet. The most concentrated solutions with which she worked contained about 30.5 grams of didymium nitrate in 10 c.c. water. She concludes that all of the facts established by her investigation can be accounted for in terms of electrolytic dissociation alone.

An excellent piece of work on the absorption spectra of aqueous solutions of neodymium chloride has recently been done by Rech.[1] The absorption bands were carefully measured as far down into the red as the sensibility of his plates would permit. There is transmission farther down into the red than could be detected by the plates which he employed.

The absorption spectra of a number of the powdered salts of neodymium and erbium were recently studied by Anderson.[2] These included the chloride, nitrate, sulphate, and oxalate. He found that each salt has its own definite absorption, which is different from that shown by any other salt.

PREPARATION OF ANHYDROUS SALTS.

When working in non-aqueous solvents, it is, of course, necessary to have the dissolved salts perfectly anhydrous. A number of the salts used in this investigation can not be dried in the air by simply raising the temperature. Under these conditions the oxy-salt would be formed. This applies to most of the chlorides and bromides, whose non-aqueous solutions were studied in this work.

In every such case the chloride in question was dried in a current of dry hydrochloric acid gas. It was placed in a porcelain boat, which was then inserted into a glass tube through which a current of dry hydrochloric acid gas was passed. The glass tube was then heated in an air-bath to the temperature required to remove all of the water from the salt.

In removing all of the water from a bromide, the salt was treated in every respect like the chloride, except that it was dried in a current of dry hydrobromic acid gas. The usual methods for testing the purity of all of the compounds employed, and of standardizing the mother-solutions of these substances, were used. A detailed discussion of this subject would be superfluous.

The praseodymium and neodymium, in the form of the double nitrate with ammonium, were furnished us, with their characteristic generosity, by the Welsbach Light Company, and it gives us unusual pleasure to express here our heartiest thanks to their chemist, Dr. H. S. Miner. The chemists of this company have always shown a spirit of coöperation with scientific work on the rare elements that is very unusual, and for which men of science, working in this field, owe them a lasting debt of gratitude.

---

[1] Dissertation, Bonn, 1906.

[2] Astrophys. Journ., 26, 73 (1907).

The praseodymium used in this work was practically free from neodymium, containing only a few hundredths of 1 per cent. From the spectrograms it would appear that the neodymium used contained about 6 per cent of praseodymium. The erbium, of course, contained quite a considerable amount of impurities.

NEODYMIUM CHLORIDE IN WATER—BEER'S LAW. (See Plates 59, 60, and 72 B.)

Five different sets of solutions were made up, covering as wide a range of concentrations as possible, the object being not only to test Beer's law thoroughly, but also to get as complete a map as possible of the absorption spectrum of neodymium chloride. In very concentrated solutions a certain group of bands may appear as a single band, due to the widening of the individual bands or to general absorption in the region considered. By diminishing the concentration such a "band" breaks up gradually into its components, and hence, to map completely the absorption spectrum, it is necessary to work over a wide range of concentrations.

If the object were simply to "map the spectrum" this could, of course, be most conveniently done by keeping the depth of layer constant and changing the concentration through a sufficient range, thus getting the complete spectrum on a single film; but since the chief object here was to test Beer's law it was necessary to make several sets of solutions covering different ranges of concentration. The concentrations of the solutions used in making the negative for A, Plate 59, beginning with the one whose spectrum is adjacent to the numbered scale, were 3.40, 3.02, 2.72, 2.38, 2.17, 1.90, and 1.70; the corresponding depths of cell being 12, 13.5, 15, 17, 19, 21.5, and 24 mm. For B, Plate 59, the concentrations were 3.40, 2.55, 1.70, 1.13, 0.80, 0.57, and 0.43; the corresponding depths of absorbing layer being 3, 4, 6, 9, 13, 18, and 24 mm. For A, Plate 60, the concentrations were 1.70, 1.27, 0.85, 0.57, 0.40, 0.28, and 0.22; for B, Plate 60, they were 0.85, 0.63, 0.42, 0.28, 0.20, 0.14, and 0.11, and for B, Plate 72, 0.42, 0.31, 0.21, 0.14, 0.10, 0.07, and 0.055; the depths of absorbing layer were in each case the same as in B, Plate 59. It will be noticed that beginning with B, Plate 59, the concentrations used in each succeeding set are just halved each time.

The most concentrated solutions appeared brownish-yellow in their bottles, from which the color changed on dilution to a yellowish-pink, the color being extremely faint in the most dilute solutions.

The exposures to the light of the Nernst lamp and spark were, respectively, 1 and 2 minutes, the slit having a width of 0.01 cm. The exposures and slit width were not varied in the work recorded in the present chapter, the object being to make the spectrograms as nearly comparable as possible.

Both A and B of Plate 59 show the presence of some general absorption in the ultra-violet, which decreases quite rapidly with dilution. The absorption bands also narrow somewhat with decrease in concentration, especially from 3.4 normal to about 1.7 normal. For concentrations less than about 1.5 normal Beer's law seems to hold very accurately indeed, with the exception of the shading towards the red accompanying the band near λ 5800, which seems to decrease somewhat with dilution for concentrations of normal or less.

In the following table the measurements of the positions of the bands were made on the seventh strip of A, Plate 59, and, therefore, refer to a concentration of 1.7 normal with a depth of layer of 24 mm. The remarks referring to changes with dilution apply to a change in concentration from 3.4 to 1.7 normal, the depths of layer being so varied that the product of concentration and depth remains constant.

λ	Character.	Remarks.
2810	Faint transmission begins.	
2890–2910	Band with well-defined sharp edges.	
2970–2995	A double band, strongest component to violet.	The observed narrowing with dilution perhaps due largely to general U.V. absorption.
3220–3330	Strong band of complete absorption, sharp edges.	Narrows slightly with dilution.
3380–3400	Rather faint band. Most intense towards red.	
3435–3595	Complete absorption. Edges sharp.	
4180	Hazy, not very intense	Narrows somewhat with dilution.
4275	Very intense and sharp	Narrows considerably at first.
4290	Narrow and faint	Between this and λ 4275 is fairly strong absorption in the most concentrated solution. This absorption has disappeared in the spectrum measured.
4330	Hazy.	
4410–4465	Edges rather hazy	This band is coincident with band due to praseodymium, and is to be ascribed to this element, which had not been completely separated from the neodymium. It does not change with dilution.
4580–4650	Band with hazy edges, not completely separated from 4665–4710.	Narrows slightly with dilution.
4665–4710	More sharply defined on red than on violet side.	Partly due to praseodymium. Does not change with dilution.
4740–4770	Fairly sharp edges	Not affected by dilution.
4820	Hazy on violet side	Due at least partly to praseodymium.
5000–5330	Red limit sharp, violet a little hazy	Violet shading a little greater in concentrated solutions.
5660–5930	Violet limit sharp. Red edge hazy	Shading on red side decreases with dilution.
6235	First and strongest band in orange group.	Not affected by dilution.
6260	Narrow and rather faint	Do.
6270–6310	Faint band	Do.
6360–6390	Faint band	Do.
6730	Faint. In shading of principal red band.	Do.
6770–6840	Principal red band. Edges hazy	Do.
6890	Band with hazy edges	Do.
7250	End of transmission	Do.

The most marked change produced by dilution from 3.4 to 1.7 normal, excepting that in the red shading of the λ 5660 to λ 5930 band, is that taking place on the red side of the narrow absorption line at λ 4275. In the spectrum of the most concentrated solution the red edge of this line falls at λ 4280, from which place a uniform absorption extends to λ 4295. In the third spectrum counting from the numbered scale, the shading has almost completely disappeared, leaving a very narrow line at approximately λ 4290. The width of this line is only 2 or 3 A.U., and it persists with unchanged intensity throughout the remaining strips of the spectrogram. Its intensity is, however, not sufficient to make it show in the reproduction, and not even great enough to make it visible on the negative for B, Plate 59.

The limits of transmission for the yellow band, as shown by the spectrum of the most concentrated solution, are λ 5660 and λ 5950; hence the narrowing of its red side amounts to 20 A.U.

B, Plate 59, starts at the same concentration as A, but the effective depth of absorbing layer is only one-fourth of that used in A. Hence this spectrogram represents the spectrum of a solution of neodymium chloride 24 mm. deep and having a concentration of 0.43 normal. The absorption bands are all much narrower, and several of them are shown in the process of breaking up into simpler bands. The bands in the ultra-violet have disappeared, excepting the one at λ 3435 and λ 3595, which is still intense, and a trace of the one at λ 3220 to λ 3330. Transmission in this region now extends faintly to λ 2460. No new absorption bands beyond λ 2800 can be seen.

The λ 3435 to λ 3595 band now has the limits λ 3450 to λ 3580, and shows a weak transmission at λ 3485, which increases somewhat with dilution, thus dividing the band into two. In A, Plate 60, this has broken up further into bands having their centers at λ 3465, λ 3500, λ 3540, and λ 3560, the bands at λ 3465 and λ 3540 being the narrowest and most intense. In B, Plate 60, λ 3465 and λ 3540 are both narrow, intense bands, while λ 3500 is faint and wide; λ 3560 disappeared entirely as a band. In B, Plate 72, the only things that remain of the group are the two narrow lines at λ 3465 and λ 3540.

The band at λ 4180 is weak throughout B, Plate 59, and may be said to have disappeared in A, Plate 60. The narrow band at λ 4275 is very persistent, showing as a fine black line even in B, Plate 72. Its width remains about the same as that shown by the negative for B, Plate 59, throughout the range of concentrations studied. The band at λ 4330 behaves exactly like the one at λ 4180, practically disappearing in A, Plate 60.

The band having its middle at λ 4445, which is perhaps entirely due to the praseodymium present as an impurity, may be seen even in B, Plate 72, although it is weak and very diffuse there. In A, Plate 59, it has about the same intensity as it shows in a solution of praseodymium chloride having a concentration of 0.85 and a depth of absorbing layer of 3 mm. This indicates that the percentage of praseodymium in the neodymium salts used was about 6 per cent. The band at λ 4825, partly due to praseodymium, may also be seen throughout the entire series under consideration, the wave-length of the praseodymium band being λ 4815, while that of the band showing in all the neodymium spectra has the position λ 4825, showing that neodymium had a band nearly coincident with that given by praseodymium, but lying a little closer to the red end of the spectrum.

The remaining praseodymium band has the position λ 4685, thus nearly coinciding with the rather narrow, strong neodymium band whose position is λ 4695. This neodymium band shows with considerable intensity even in Plate 72 B, while the praseodymium band at λ 4685 is so much fainter than the λ 4445 band due to the same substance that we should hardly expect it to show here.

The band which under A, Plate 59, was recorded as having the limits λ 4580 to λ 4650 shows in B as a hazy band with its center at λ 4615, together with a narrow, faint line at λ 4645. The band is visible in A, Plate 60, but has practically disappeared from view in B, of the same plate. The narrow line at λ 4645 does not show beyond B, Plate 59.

The band which in the table is recorded as λ 4740 to λ 4770 has in B, Plate 59, become a slightly hazy band having its middle at λ 4760. Its intensity is intermediate between that of the bands at λ 4695 and λ 4825, and, hence, like them may be seen faintly even in B, Plate 72.

The band which in A, Plate 59, has the limits λ 5000 to λ 5330 breaks up into a rather complicated series of bands on dilution, some idea of which may perhaps be gained from the following: B, Plate 59, shows some absorption throughout the region given, but with a deep, narrow band at λ 5090 and faint transmission at λ 5100 and in the region λ 5150 to λ 5180. Absorption is complete from λ 5105 to λ 5150, and from λ 5180 to λ 5270. There is again incomplete absorption from λ 5270 to λ 5330, with indication of a band at λ 5315. In A, Plate 60, the general shading has the limits λ 5050 to λ 5330, and it shows the following: A narrow intense band at λ 5090; wide, hazy band at λ 5125; a pair of very intense, narrow bands at λ 5205 and λ 5222; very narrow band at λ 5255; and faint, hazy band at λ 5315. B, Plate 60, shows the shading diminished very much in intensity, and all the bands except the doublet λ 5205 to λ 5222 rather faint. The absorption in the doublet is still almost complete. B, Plate 72, still shows the doublet very strong, the remaining absorption bands faint, although still visible.

The limits of the yellow band in B, Plate 59, are λ 5700 to λ 5880 in the strip corresponding to the most concentrated solution. The band narrows by 30 Ångström units on this spectrogram, the narrowing being due to a decrease in the shading towards the red, with decrease in concentration. In B, Plate 60, the limits of the band are λ 5710 and λ 5840. There is still considerable shading, but it decreases only very slightly with dilution. The band begins to show its structure, but not well enough to allow any measurements to be made.

In B, Plate 60, and B, Plate 72, the band has broken up into the following smaller bands: λ 5725, narrow and moderately intense. λ 5745 and λ 5765, double band, not clearly resolved, the red component being more intense than the violet. This double band is the most intense of the group. λ 5795, band having about the same intensity as the one at λ 5725, but being much wider and hazier. λ 5380, very faint band.

The group of absorption bands in the orange, given in the table, may be seen faintly in B, Plate 59, and very faintly in A, Plate 60; but, like the group in the red near λ 6800, it shows no further breaking up into more complicated bands on dilution.

B, Plate 59, shows that the spectrum ends at λ 7310 in what appears to be an absorption band. In Plate 60, and B, Plate 72, it is seen that there is a very intense, narrow band at λ 7325; another narrow but fainter band at about λ 7350, and a wide, moderately intense band at λ 7390 or λ 7400, beyond which the plates were not sufficiently sensitive to give any appreciable photographic action with the length of exposure used.

The most intense bands of neodymium chloride, and hence the ones which would be most conspicuous in a very dilute solution, are the following: λ 3465, λ 3540, λ 4275, λ 5205, λ 5225, λ 5745, λ 5765, and λ 7325.

The wave-lengths of all the bands are collected in the following table, together with a brief description of the appearance of each band. It is to be understood that this table is not meant to represent what could be seen or photographed in any one solution of neodymium chloride in water. It merely records the position of all the bands which can be seen in a layer from 3 to 12 mm. deep, when the concentration is varied from 0 to 3.4 normal.

λ	Character.	λ	Character.
2900	About 20 A.U. wide.	5205	Very intense, narrow.
2985	About 25 A.U. wide.	5222	Very intense, narrow.
3225	Narrow and sharp.	5255	Narrow, intense.
3390	Narrow, faint.	5315	Hazy edges, faint.
3465	Very intense, narrow.	5725	Narrow, intense.
3505	Rather wide.	5745	Very intense.
3540	Very intense, narrow.	5765	Very intense.
3560	Faint, narrow.	5795	Intense, moderately narrow.
4180	Faint, hazy.	5830	Very faint and hazy.
4275	Very intense and sharp.	6235	Fairly narrow.
4290	Very narrow, faint.	6260	Very narrow, faint.
4330	Hazy edges.	6270–6310	Faint, hazy edges.
4615	Rather wide and hazy.	6360–6390	Faint, hazy edges.
4645	Very narrow, faint.	6730	Faint band.
4695	Narrow, intense.	6800	Moderately intense, hazy edges.
4760	Hazy edges, fairly narrow.	6890	Hazy edges.
4825	Narrow and fairly intense.	7325	Very intense and narrow.
5090	Narrow, intense.	7390	Rather wide band.
5125	Rather wide and hazy.		

NEODYMIUM CHLORIDE IN WATER—MOLECULES CONSTANT. (See Plate 61.)

The dissociation of neodymium salts not having been determined, it was assumed that their dissociation was the same as those of aluminium. Although this may not be exactly true, yet the rate of change of dissociation with concentration will perhaps be practically the same for the two metals, and that is the only thing which comes into account here.

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 3.4, 2.7, 1.95, 1.44, 1.10, 0.86, and 0.69; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 1.36, 1.10, 0.80, 0.59, 0.44, 0.35, and 0.28; the depths of the absorbing layers were the same as in A.

Since Beer's law holds so very accurately for neodymium chloride in water, excepting at the very greatest concentrations, it is to be expected that when molecules are kept constant all the bands would show considerable widening with dilution, and this is found to be the case. It will be recalled, however, that the shading on the red side of the yellow band showed considerable deviations from Beer's law, even at moderate dilutions; and it was to see whether there is any connection between this shading and the undissociated molecules that the present spectrogram was made. Here it will be seen that the shading decreases when the concentration is changed from 3.4 to 1.95, then remains sensibly constant until the concentration becomes as small as about 1.0, when it increases with further dilution. It seems evident, then, that this shading can not be ascribed to the undissociated molecules, any more than can the rest of the absorption phenomena shown by these solutions. Apparently the absorption depends only upon the number of neodymium atoms present, and is independent, or nearly so, of whether these exist as ions or combined with chlorine to form the chloride molecules.

NEODYMIUM CHLORIDE IN WATER WITH CALCIUM CHLORIDE AND WITH ALUMINIUM CHLORIDE. (See Plate 62.)

The concentration of neodymium chloride in all the solutions was the same, namely 0.23. The concentrations of calcium chloride, beginning with the solution adjacent to the numbered scale of A, were 4.29, 3.68, 2.86, 2.29, 1.72, 1.14, 0.57, and 0.0; the corresponding concentrations of aluminium chloride in the solutions used in making the negative for B being 2.80, 2.40, 2.00, 1.60, 1.20, 0.80, 0.40, 0.00. Depth of absorbing layer throughout, 2.0 cm.

These dehydrating agents, especially the aluminium salt, introduce considerable general absorption in the ultra-violet. This, however, is due to the foreign salt itself, and is in no way to be ascribed to its effect on the neodymium salt in the solutions. This general absorption also accounts for the apparent increase in intensity of the ultra-violet absorption band of neodymium at λ 3500.

The shading on the red side of the yellow band is slightly increased by the addition of calcium chloride, and somewhat more so by the addition of the aluminium salt. Beyond this no effect on the absorption spectrum of neodymium chloride is produced by even large quantities of these dehydrating agents.

NEODYMIUM CHLORIDE IN METHYL ALCOHOL—BEER'S LAW. (See Plate 63.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.50, 0.40, 0.315, 0.25, 0.20, 0.16, and 0.125; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. The concentrations for B were, in the same order, 0.20, 0.16, 0.13, 0.10, 0.08, 0.06, and 0.05; the depths of cell were the same as used in A.

There is some absorption in the extreme ultra-violet, which, however, is to be ascribed to the solvent and not to the neodymium chloride.

No trace of absorption due to the dissolved substance is visible until we reach the group of bands near λ 3500. There are three bands having their centers at λ 3475, λ 3505, and λ 3560. Of these the one at λ 3560 is the widest and also the most intense; the one at λ 3475 being somewhat fainter than that at λ 3505. The bands are all much wider and hazier than those occurring near the same place in the aqueous solution. No change with dilution indicating a deviation from Beer's law can be detected in these or any of the other bands in the alcoholic solutions of the chloride.

In the violet and blue regions we find the following : A band at λ 4290, about 10 A.U. wide and only moderately intense. At λ 4325, a band somewhat wider and fainter. At λ 4460, a rather wide hazy band with a faint hazy companion towards the violet. This is the band which is perhaps due to praseodymium. The much greater concentration of the alcoholic solutions of praseodymium chloride studied in this work makes it impossible to verify this, by seeing whether the praseodymium band in dilute solution really has this general character.

There are bands at λ 4700, λ 4780, and λ 4825, all of about the same intensity, the one at λ 4770 being, however, much narrower than the other two, of which λ 4825 is somewhat the wider. Both λ 4700 and λ 4780 have faint companions to the violet.

The group in the green is made up of six bands as follows : λ 5125, hazy and rather wide, moderately intense; λ 5180, also hazy but much fainter; λ 5220, moderately intense and narrow; λ 5245, intense, and with faint companion towards the red; λ 5290, narrow and moderately intense; shading as far as λ 5330, with indications of a faint band at λ 5315.

The yellow group is made up of seven bands having the following characteristics : λ 5725, moderately intense with hazy edges ; λ 5765, narrower, but not quite as intense as λ 5725; λ 5800, fairly narrow, strong; λ 5835, very intense; λ 5860, hazy and moderately intense, not clearly separated from λ 5835, shading to λ 5970, with two faint bands superimposed upon it, one at λ 5895 and the other at λ 5925.

No trace of bands is to be seen in the orange, but in the red there is a fairly narrow but faint band at λ 6860. The spectrum ends at λ 7355 in a deep, rather narrow band. It is evident that the spectrum of neodymium chloride when dissolved in methyl alcohol is quite different from its spectrum in aqueous solution, but this point will be taken up more fully in the discussion of Plates 65 and 66.

NEODYMIUM CHLORIDE IN ETHYL ALCOHOL—BEER'S LAW. (See Plate 64.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.50, 0.40, 0.315, 0.25, 0.20, 0.16, and 0.125 ; the corresponding depths of absorbing layer being 6, 7.5, 9.5, 12, 15, 19, and 24 mm. For B, the concentrations were 0.20, 0.16, 0.13, 0.10, 0.08, 0.06, and 0.05; the depths of cell were the same as used in A. The concentrations and depths of cell were, therefore, exactly the same as those in methyl alcohol, so that Plates 63 and 64 are directly comparable. A very careful comparison of the two plates reveals the remarkable fact that the two spectra are identical; the very slight differences noted being perhaps due to slight differences in development of the negatives.

In view of the great difference between either one of these spectra and that of the aqueous solution, this similarity is rather surprising, and it led us to think that perhaps in these alcoholic solutions we were getting the absorption of the neodymium chloride molecules themselves, while in the aqueous solution we get the absorption of some compound of the molecules with water. But this was answered in the negative by the spectrum of anhydrous neodymium chloride (Plate 68), which is very different from that of any of the solutions. The spectrum of the alcoholic solutions is, therefore, not that of the $NdCl_3$ molecule *per se*, but must be that of some solvate of it or of the neodymium ion. But that solvates with methyl alcohol and ethyl alcohol should affect the frequencies of the vibrators in the metallic atom so very nearly the same seems a little surprising, to say the least, especially as solutions of the nitrate in the two solvents give somewhat different spectra, as will be fully discussed when we come to consider Plates 73 and 74.

The very slight differences between the bands shown by Plates 64 and 63 seemed to indicate that they were a little more hazy in the ethyl alcohol solutions, but the development of the negatives for Plate 64 was not carried quite as far as was the case with those for Plate 63, and this would tend to produce just the kind of difference that was noted.

NEODYMIUM CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND WATER.

(See Plates 65, 66, and 76 B.)

Since, as we have just seen, the absorption spectrum of neodymium chloride in aqueous solution is so different from that of the alcoholic solutions, *it was thought to be of some interest to see how the change from the one to the other would take place if one of the solvents was made to displace the other gradually.* A series of solutions was accordingly made up, the concentration of the dissolved salt being constant and equal to 0.5 normal, but the character of the solvent varying as follows : The percentages of water in the seven solutions were 0, 16.6, 33.3, 50, 66.6, 83.3, and 100; the corresponding percentages of methyl alcohol were 100, 83.3, 66.6, 50, 33.3, 16.6, and 0. Two spectrograms were made, namely, A, Plate 65, where the depth of the cell was 1.5 cm., and B, where the cell had a depth of only 5 mm. A was made in order to show clearly the change taking place in the narrower and fainter bands, while B was intended to show the change of structure of the more intense bands, such as the green and yellow ones. The strip which is adjacent to the numbered scale belongs to the solution in pure water, while the one nearest the narrow, comparison spark spectrum belongs to the solution in pure methyl alcohol.

Plate 65 shows that, beginning with the strip nearest the scale, the first six spectra are very nearly identical. From the sixth to the seventh there is an abrupt change, which at first sight consists in a shift of all the bands towards the red, but which on closer examination is seen to consist in a disappearance of one spectrum and the appearance of the other. Since the first strip is the spectrum of the solution in pure water, it follows, since the sixth is nearly identical with the first, that as large a percentage of alcohol in the solvent as 83 per cent does not change the absorption spectrum materially; the chief change taking place when the percentage of alcohol is varied from 83 per cent to 100 per cent.

It is to be noted that the apparent shift of the bands towards the red is in reality not quite as great as it appears at first sight from Plate 65, owing to the fact that the film accidentally shifted slightly towards the red between the sixth and seventh exposures. The amount of this mechanical shift is easily seen, however, by comparing the spark lines in the ultra-violet. A measurement of the shift shows it to be approximately 3 Ångström units, and the same for both A and B, while the "apparent" shift of the absorption line at λ 4275 in aqueous solution is actually 15 Ångström units, its position in the alcoholic solution being λ 4290.

The slight changes taking place with some of the bands throughout the spectrograms of Plate 65 are perhaps sufficiently clear in the reproductions. However, as a good deal of the detail shown by the negatives is lost, even in the most perfect processes of reproduction, we give here a description of the changes taking place in two of the bands as seen on the original negative. We select the bands at λ 4275 and λ 4760 from the negative for A, Plate 65.

In the aqueous solution the λ 4275 band is very intense and narrow, its whole width being less than 5 Ångström units. The edges are only very slightly shaded. In the alcoholic solution the position of the center of the corresponding band is λ 4290. It has a width of from 12 to 13 Ångström units, and is not nearly as intense as in the aqueous solution.

Throughout the first six strips the λ 4275 band maintains its position and intensity almost unchanged. Its position does not change in the least, but its intensity in the sixth strip is a trifle less than in the others. In the seventh strip there is not the faintest trace of it left. In the third strip, corresponding to the solution whose alcohol content was 33.3 per cent, there appears at λ 4285 an extremely faint and narrow line. In the fourth strip it is somewhat wider and more intense, but its center is still at λ 4285. In the fifth strip it is beginning to be fairly conspicuous, and in the sixth it is a band of moderate intensity, having its center at about λ 4287. This band is undoubtedly the same one which in the pure alcoholic solution has its center at λ 4290 or very near there, the exact wave-length being perhaps nearer to λ 4292. We see, then, that even when the mixed solvent contains only about one-half alcohol, this band exists independent of and distinct from the band characteristic of the aqueous solution; that it is at first only a very narrow and faint line, which widens towards the red as the percentage of alcohol is increased.

The band whose center is at λ 4760 has the following appearance in the aqueous solution: Faint absorption begins at λ 4748 and rises rapidly to a maximum between λ 4755 and λ 4760, then decreases slowly to nothing at λ 4775. The band is accordingly a trifle asymmetrical, the slope towards the violet being considerably steeper than that towards the red. The corresponding band in the alcoholic solution is double and answers the following description: Very faint absorption begins at λ 4753, and rises to a faint maximum at about λ 4757, becoming again zero at λ 4760. It begins again at λ 4772, rises rapidly to a strong maximum at λ 4780, and falls to zero at λ 4790. The component whose center is at λ 4757 is very faint compared with the main band.

In the first and second strips we have nothing but the band corresponding to the aqueous solution. In the third strip the red side of the band has increased slightly in intensity, making it appear much more nearly symmetrical. This change increases in the fourth and fifth strips, the band at the same time widening considerably. In the sixth strip its appearance is as follows: Absorption begins at λ 4748 and rises to a maximum just to the violet side of λ 4760, then decreases slightly towards λ 4770, after which it increases somewhat to λ 4778, then falls off to zero at λ 4787. It is very evident from a study of the change in this band that *the two bands characteristic of the aqueous and alcoholic solutions coexist,* and that the band appearing in our photographic strip is the sum of the two taken in different proportions, the proportion of the alcohol band being, however, very much smaller than the proportion of alcohol in the corresponding solution. A similar description might be given for any one of the other bands, but this is not necessary, as the changes are of exactly the same nature as those we have already indicated. In every case where the alcoholic solution has a strong band which differs somewhat in position from any band in the aqueous solution, we begin to see traces of this band when the proportion of alcohol in the mixture reaches 50 per cent; but the band remains comparatively faint even when the proportion is as high as 83.3 per cent.

In order to study the change that takes place between the sixth and seventh strips of the spectrograms of Plate 65 more carefully, a series of alcoholic solutions was prepared containing the following percentages of water, 0, 2.6, 5.3, 8, 10.6, 13.3, and 16. The concentration of the neodymium chloride was constant and equal to 0.5 normal. Two spectrograms were made, one with a depth of absorbing layer of 1.5 cm. in order to show the fainter bands, and the other with the depth of the cell only 5 mm. in order to show as much as possible of the structure of the larger bands. The first spectrogram is reproduced as Plate 66 A and the second as Plate 66 B. The strips corresponding to the pure alcohol solutions are adjacent to the numbered scale, the spectrum of the solution containing 16 per cent water being next to the comparison spark spectrum.

Although we found on considering Plate 65 that some slight change in the spectrum takes place when the percentage of alcohol is changed from 0 to 83 per cent, yet this change is so small, and the bands due to the aqueous solution are so strong, that we may regard the spectrum of a solution containing 16 per cent of water as practically that of the aqueous solution. Accordingly, the spectrograms on Plate 66 may be taken to show very nearly the whole change which takes place when the solvent of neodymium chloride is gradually changed from pure water to pure methyl alcohol.

In A the ultra-violet band is rather too intense to allow its structure to be seen. Accordingly, we see the whole band remain sensibly unchanged as the water is varied from 16 per cent to 8 per cent, and then shift towards the red with increasing rapidity as the water is reduced to zero, the whole apparent shift amounting to about 20 Ångström units. On the negative the intense band at λ 3465 may, however, be clearly seen, and its intensity decreases very slowly from the first to the third strips, counting from the narrow, comparison spark spectrum. In the fourth strip its intensity is about half of what it was in the first strip, and from this it decreases rapidly, vanishing entirely in the strip nearest the scale.

In B the structure of this band is seen very distinctly, and we find that the bands characteristic of the aqueous solution gradually decrease in intensity, especially from the third to the sixth strips, while the wider bands, characteristic of the alcoholic solutions, increase in intensity, the two sets existing together. The change in the band at λ 4275 is the one that shows the best, because here the two bands belonging to the aqueous and alcoholic solutions, respectively, are both intense and narrow and clearly separated from one another.

The alcoholic band is clearly visible in the first strip, and it increases continuously in intensity as the amount of water is decreased, but more rapidly from the fourth to the seventh strips than from the first to the fourth. Its position also shifts somewhat towards the red from the first to the fourth strips, the wave-lengths of its center for the two strips being, respectively, λ 4287 and λ 4292. Accompanying this shift is a change in its character, which may be gathered from the following statements: In the first strip it has the appearance of an unsymmetrical band, the maximum intensity being nearer the violet. In the third strip it extends from λ 4280 to λ 4295, and has about the same intensity throughout. In the fourth strip the intensity of its violet edge has decreased while that of the red edge has increased considerably, giving it the appearance of an unsymmetrical band, with the maximum intensity towards the red. In the fifth strip the violet shading from λ 4280 to about λ 4284 has disappeared, leaving a band very nearly symmetrical about λ 4290. It appears, therefore, that we are really dealing with two unresolved bands, one having its center at about λ 4285 and the other at λ 4292.

The band at λ 4275, due to the aqueous solution, decreases in intensity throughout, but more rapidly from the third to the sixth strips than at first. Its position remains the same throughout. As near as the eye can judge this band has had its intensity reduced to about half value, when the fourth strip is reached, corresponding to 8 per cent of water in the solution. The alcohol band at λ 4292 also has about 50 per cent of its final intensity in the same solution.

The band at λ 4760 shows the same kind of a change that we described in some detail above, only here the change is much more gradual and easy to follow. It also shows about equal intensity for the two sets of bands when the amount of water is 8 per cent of the whole.

The green and yellow bands are not sufficiently resolved in A to allow the change in the individual bands to be followed, and hence these apparently show only a gradual shift towards the red with decrease in the amount of water. In B, however, they are both sufficiently resolved to enable us to follow the change in each individual band, which, although a little difficult on account of their large number and the incompleteness of their separation, in some cases may still be done. The change is in every respect the same as we have found for the other bands, namely, those due to the aqueous solution diminish in intensity, and reach about half value in the 8 per cent water solution, while those belonging to the alcoholic solution increase in intensity as the amount of water is decreased.

The band in the red near λ 6800 shows the change very well indeed, the "water" band having the position λ 6800, while that pertaining to the alcoholic solution is situated at λ 6860, and hence the two are well separated. Here the point of equal intensity appears to be reached in the solution containing 10.6 per cent of water, but this is due to the fact that the alcoholic band has a considerably greater intensity than that due to the aqueous solution, conditions as to concentration and depth of layer being the same. Taking this into account, it is seen that this band obeys substantially the same rule as the others.

The change in the band at λ 7325 is more difficult to follow on account of the small intensity of the photographic action on the less refrangible side of this position. The band belonging to the aqueous solution may be seen very clearly, even in the strip corresponding to the 2.6 per cent water solution, but is, of course, entirely absent in the alcoholic solution. Its intensity in the 2 per cent solution, however, seems a little greater than we should expect from the behavior of the other bands, but this is perhaps due to the rather weak photographic action in this part of the spectrum, combined with the great intrinsic intensity of the band. The alcoholic solution transmits light as far as λ 7355, where its spectrum ends abruptly in a band.

Throughout this description we have laid great stress on the fact that on Plate 66 the *two sets of bands coexist, the bands due to the aqueous solution decreasing, while those belonging to the alcoholic solution increase in intensity with decrease in the percentage of water;* we have also called attention to the fact that the two sets of bands have about half their full intensity in a solution containing about 8 per cent of water. This was for a 0.5 normal solution.

The next question which suggested itself was whether the composition of the solvent, in order to give the two sets of bands with about half their normal intensity, is independent of the concentration of the dissolved substance. If this be independent of the concentration, then we should have to conclude that the determining factor is the nature of the solvent; while if it depends upon the concentration, the ratio between the amount of dissolved substance and one or other of the solvents would perhaps be the important thing. To answer this question a set of solutions was made up, keeping the solvent exactly the same as it was for the solutions used in making the negatives for Plate 66, but making the concentration of neodymium chloride 0.25 normal instead of 0.5 normal. The resulting spectrogram is shown in Plate 76 B. In order to have this spectrogram directly comparable with B, Plate 66, the depth of cell was kept at 1.0 cm. throughout.

A study of this negative shows that the two sets of bands have about half their normal intensity in the third strip, counting from the numbered scale, corresponding to 5.3 per cent of water. In the fourth strip the bands characteristic of the alcoholic solutions are very weak compared with the bands belonging to the aqueous solution, while in the second strip the opposite is the case. It is plain, therefore, that the composition of the solvent, in order that the two sets of bands may show with about half their normal intensity, depends upon the concentration, and it also seems very probable that, provided the ratio of water to dissolved substance is kept constant, the two sets of bands will not vary much in relative intensity. A simple calculation shows that in the solutions which produced the bands with about half their normal intensity, there were present approximately 10 molecules of water to 1 molecule of neodymium chloride.

NEODYMIUM CHLORIDE IN ETHYL ALCOHOL WITH WATER. (See Plate 67 A.)

The concentration of neodymium chloride was constant and equal to 0.5 normal. The percentages of water, beginning with the solution whose spectrum is adjacent to the numbered scale, were 0, 5.3, 10.6, 16, 21.3, 26.6, and 32. The depth of the cell throughout was 0.5 cm.

This spectrogram shows exactly the same kind of change that we have considered rather fully under Plate 66. The increments of water added were twice as large here as in the case of methyl alcohol, and hence the change takes place more rapidly as we pass from strip to strip, beginning with the one next to the numbered scale. It is seen that in the second strip the bands characteristic of the alcohol solution are very much more prominent than those belonging to the water solution, while in the third strip the reverse is true. This points to the fact that here too the composition of the solvent, in order to give the bands with about half their normal intensity, would be 7 or 8 per cent water and the rest alcohol. In other words, we again find complete agreement between solutions of neodymium chloride in the two alcohols.

If the fact described under the last heading, that the relative intensities of the two sets of bands depend only upon the ratio of water to neodymium chloride in solution, should be found to hold even for concentrations of one-tenth or one-hundredth of those employed here, this ought to furnish a very convenient optical method of detecting rather small quantities of water in alcohol; for it is apparent that with a quarter normal solution, 1 per cent of water gives the bands due to the aqueous solution with sufficient intensity to be seen easily with a small spectroscope if a layer of a centimeter or so in depth is used. Accordingly, to detect an amount of water as small as 0.01 per cent, it would only be necessary to dissolve in the alcohol enough anhydrous neodymium chloride to make a $\frac{1}{250}$ normal solution, and fill a glass tube with the solution, so as to get a layer from 50 to 100 cm. deep, when the bands due to water should easily be seen.

NEODYMIUM CHLORIDE—ANHYDROUS. (See Plate 68.)

This plate was made in order to see whether the spectrum of the anhydrous salt is identical with that observed when the salt is dissolved in pure methyl or ethyl alcohol. The anhydrous salt was in the form of a very fine powder, and contained in a bottle with a tight-fitting glass stopper. An image of the Nernst filament was thrown on the surface of the powder in contact with the walls of the bottle, and this image was in turn focussed on the slit of the spectroscope by means of the concave spectrum mirror. The light falling on the grating was necessarily very faint; therefore, rather long exposures were necessary; but this caused no inconvenience, since the Nernst lamp burns so steadily that it needed no attention whatever. In order to show as well as possible both the strong and the weak bands, a series of exposures were made on the same film, the times of exposure, beginning with the strip nearest the numbered scale, being 30 minutes, 1 hour, 1½ hours, 2 hours, and 2½ hours. On account of the fact that the beam of light had to pass through the glass condensing lenses, as well as the glass walls of the containing bottle, the spectrum ends at about λ 3450 for the strip nearest the comparison spectrum, and at λ 3600 for the one nearest the scale.

The comparison spark spectrum in this case was made by using zinc terminals instead of the carbon terminals employed throughout the rest of the work. Since there is usually some accidental shift between the successive strips on a film, and since no light but that of the Nernst filament was used in making the five strips on Plate 68, it is evident that no accurate wave-length measurements could be made by a comparison with the spark spectrum on this plate. In fact, the position of a given absorption line, which appeared both on the film and on the red-sensitive plate, was found to differ by as much as 10 Ångström units as measured from the two negatives. Hence it was necessary to determine the position of one or more of the absorption lines by comparison with a spark spectrum which should have been impressed on the plate without moving this between the exposures to the light reflected from the chloride powder and to that from the zinc spark. This was accomplished by making an exposure of about an hour for the absorption spectrum and then, without moving the plate holder, impressing the ultra-violet portion of the spark spectrum on the same strip. Thus, the position of a few of the strongest and sharpest absorption bands was determined, and the positions of the others were measured by determining their distances from the standards.

On the whole, the spectrum is similar to that observed in solutions; that is, if the solutions show a group of absorption bands in a certain region, then there is also a group of bands in nearly the same place in the spectrum of the light reflected from the anhydrous salt; but as a rule the individual bands in the group are much narrower and more numerous in the latter than in the former. This agrees with what has previously been found by Becquerel[1] and by one of us.[2]

In the following table, the position and character of the stronger bands are given. No attention was paid to the numerous bands that are so faint as to require special precautions in order to study them, as the object of the present work was not so much the cataloguing of the spectra as to try to get some idea of the causes of the changes which take place when the substance is subjected to different conditions.

λ	Character.	λ	Character.
3500	Rather strong, narrow band.	5183	Not as narrow as 5174.
3537	Weaker and wider.	5216	Shaded to violet.
3570	Narrow and intense.	5254	Very intense and narrow.
3595	Narrow and very intense.	5267	Very intense and narrow.
3612	Rather faint and hazy.	5282	Weaker and wider than the last two.
4045	Weak and hazy. Perhaps 2 or 3 bands.	5300	Shaded towards red, perhaps double.
4080	More intense, but hazy.	5328	Intense, narrow.
4210	Faint, narrow.	5342	Weaker and broader.
4228	Faint, perhaps 2 bands.	5760–6000	Strong general absorption.
4308	Very narrow and intense.	5768–5782	Very intense, double band.
4313	Very narrow and intense.	5807	Narrow and intense.
4333	Wider and a little hazy, but intense.	5829	Most intense band in spectrum.
4357	Narrow, shaded towards red.	5858	Very narrow.
4455	Wide and hazy.	5875	A little hazy.
4500	Wide and hazy.	5890	Weak.
4640	Faint, hazy.	5902	Fairly narrow and intense.
4680	Faint, hazy.	5922	Hazy and faint.
4717	Narrow and moderately intense.	5946	Narrow, intense.
4725	Narrow and moderately intense.	5968	Wide, faint and hazy.
4735	Narrow and moderately intense.	6265	Wide, moderately intense.
4775–4790	Sharp on violet side, perhaps 2 bands.	6290	Narrow, faint.
4815	Rather narrow.	6325	Narrow, faint.
4855	Intense and narrow.	6375	Narrow, faint.
4872	Weak.	6775	Wide, faint.
4888	Narrow, moderately intense.	6796	Narrow, faint.
4895	Narrow, moderately intense.	6815	Narrow, faint.
5000–5370	Strong general absorption.	6838	Moderately intense.
5088	Weak, slightly hazy.	6860–6900	Band, shading towards red.
5117	Stronger, shaded somewhat.	6922	Moderately intense.
5147	Narrow, intense, hazy on violet edge.	7422	Narrow, intense band.
5174	Intense, slightly hazy.		

It is, of course, evident that the spectrum of the solutions of neodymium chloride dissolved in methyl or ethyl alcohol is very far from being that of the anhydrous salt. It seems reasonable to suppose that if the molecules of the salt in the non-aqueous solutions exist in the free state, that is, not combined with the solvent in any way, they should give about the same spectrum as they do when in the state of the dry powder. Since they do not do this, *we must suppose that the solvent plays an important rôle in determining the character of the absorption, and how it can do this without being combined with the salt in some way is not easy to understand.*

---

[1] H. Becquerel, Ann. Chim. Phys. (6), 14, pp. 257 et seq.

[2] J. A. Anderson, Astrophys. Journ., 26, Sept., 1907, pp. 73–94.

Neodymium Bromide in Water—Beer's Law. (See Plate 69.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.3, 1.7, 1.15, 0.77, 0.54, 0.38, and 0.29; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.57, 0.42, 0.29, 0.19, 0.13, 0.09, and 0.07; the depths of the absorbing layer were the same as in A.

The bromide solutions are very much redder in color than those of the chloride or nitrate. Judging from the color alone, one would say that the nitrate solutions are much more transparent in the blue and violet than the chloride, and the chloride solutions much more so than those of the bromide. The spectrograms do not show this, at least not very clearly; which merely indicates that where full exposures are given, slight general absorption is not recorded by the photographic plate. A spectrophotometric comparison of the light transmitted through these solutions, such as is now in progress in the present work, will undoubtedly show this general absorption of the bromide solutions in the more refrangible portion of the spectrum.

In studying the spectrograms of this plate, A was compared with Plate 59 B, and B with Plate 60 B, that is, the spectrum of the bromide solutions was compared with that of a chloride solution whose concentration, in each case, was almost exactly 1.5 times that of the bromide solution, the depth of the absorbing layer being the same in both cases. The two spectra were found to be almost identical, except in the extreme ultra-violet, where the bromide solutions absorb much more strongly. The limits of transmission for the most concentrated and most dilute solutions of A are, respectively, λ 3270 and λ 3050; whereas the corresponding chloride solutions transmitted to beyond λ 2500. The ultra-violet absorption shown by B is about the same as that of the chloride solutions used in making Plate 59 B.

The absorption bands have in general about the same intensity and character in the bromide solutions as they have in the corresponding solutions of the chloride, indicating a considerably greater absorbing power of the bromide, since the concentrations of its solutions were only 0.66 of that of the chloride. A small part of this is due to the fact that the negatives for Plate 69 were not as fully developed as those made with the chloride solutions, but even if the development had been exactly the same, the bands of the bromide solutions would only have been very slightly less intense than those of the chloride solutions. We must, therefore, conclude that in solutions of the same concentration the bands of the chloride solution would have only about 75 per cent of the intensity of the same bands in the spectrum of the solution of the bromide.

It will be remembered that the very concentrated solutions of the chloride showed some slight deviations from Beer's law, the absorption to the red side of the narrow band at λ 4275 being described in some detail. The deviations from Beer's law are smaller in the bromide solutions, perhaps on account of the concentrations being less. No shading or fine absorption line between λ 4275 and λ 4290 is to be seen in the spectra of even the most concentrated solutions used in making the negative for A of Plate 69. The shading on the red side of the yellow band narrows somewhat with increasing dilution, but not quite as rapidly as was the case with the chloride.

Some neodymium bromide was dehydrated in a current of hydrobromic acid and dissolved in methyl alcohol, and also in mixtures of methyl alcohol and water. The solution in methyl alcohol was stable, and showed the same spectrum as a solution of the chloride in the same solvent. On adding water, precipitates were formed, indicating some chemical change. These were filtered out, and a spectrogram made to see whether the same changes take place in this case that we observed with the chloride. This spectrogram is not reproduced, but it indicated that the changes which took place were quantitatively as well as qualitatively the same as those which we discussed under Plates 65 and 66.

NEODYMIUM NITRATE IN WATER—BEER'S LAW. (See Plates 70 and 71.)

The concentrations of the solutions used in making the negative for A, Plate 70, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.96, 2.22, 1.48, 0.99, 0.69, 0.50, and 0.38. For B the concentrations were 1.48, 1.11, 0.74, 0.50, 0.35, 0.25, and 0.19. For A, Plate 71, they were 0.74, 0.55, 0.37, 0.25, 0.175, 0.125, and 0.095; and for B, 0.37, 0.275, 0.185, 0.125, 0.092, 0.062, and 0.048. The depths of absorbing layer were in each case 3, 4, 6, 9, 13, 18, and 24 mm.

The nitrate solutions are much less yellow than the chloride solutions, having when concentrated a decided pinkish tint, indicating greater transparency in the violet region of the spectrum.

The spectrum of the nitrate solutions, especially when the concentration is considerable, differs quite a little from that of the chloride. It is true that at first glance they seem identical, for wherever there is a band in the spectrum of the chloride solution a band is found when the nitrate solution is examined; but, at least in concentrated solutions, the bands have a very different appearance. The general difference is that the nitrate bands are much broader and hazier than those observed with the chloride. With dilution the spectrum of the nitrate changes very much more than that of the chloride, which we found practically unaltered when the concentrations were changed from about 1.5 normal nearly to zero. The spectrum of the nitrate solutions changes somewhat, even in B, Plate 71, where the concentration ranges from 0.37 to 0.048 normal.

Instead of giving a detailed description of the spectrum of the nitrate, we will limit ourselves to a description of the changes that take place in a few of the bands, which differ most from the corresponding bands in the spectrum of the chloride solution.

Let us consider first the band at λ 4275. In the spectrum of the chloride solution this band has the width of only a few Ångström units and is very intense. In the most concentrated nitrate solution this band has a width of 15 A.U. and its center falls at about λ 4280. Its edges are rather hazy, but the band is very symmetrical. With increasing dilution the violet edge increases in intensity, taking more and more the form of a narrow absorption line with center at λ 4275; while the red portion of the band decreases in intensity, and at a concentration of 0.38 and a depth of layer of 24 mm. it has taken the form of a slightly hazy band with its center near λ 4282. This band is here clearly separated from the more intense and narrower one at λ 4275. With a concentration of 0.19 normal and a layer 24 mm. deep, the λ 4282 band has become a mere shade on the red side of the λ 4275 band; and finally, with a concentration of 0.048 and a 24 mm. layer of the solution, it is no longer visible on the photograph.

At λ 4330 or λ 4335 the concentrated chloride solutions show a rather wide hazy band, the intensity of which is not sufficient to allow it to be seen in solutions of less than 1.0 normal with a depth of layer of 5 mm. or less. The more dilute solutions of the nitrate used in making A, Plate 70, show this band with about the same intensity and character that it has in solutions of the chloride; while the very concentrated nitrate solutions show it very faintly; that is, the band increases in intensity with dilution. In fact it behaves very much like the λ 4275 band, indicating that the two owe their origin to the same "absorber."

The 3.4 normal chloride solution in a layer 3 mm. deep, shows a band at λ 4760, to which the following description applies : Absorption begins at λ 4750, rises gradually to a maximum at λ 4760, then gradually falls to zero at λ 4770. This band remains practically constant throughout the series of solutions used in making B, Plate 59, showing that it is practically unaffected by change in concentration.

The 2.96 normal solution of the nitrate, with a layer 3 mm. deep, shows a band in the same region which has the following characteristics : Absorption begins at λ 4730, rises to a maximum at λ 4737, then falls to a slight minimum at λ 4742, from which it again rises to a maximum at λ 4755, falling off gradually to zero at λ 4780, with indications of a faint minimum near λ 4765. We really have to deal with a group of three bands then, their centers being approximately at λ 4737, λ 4755, and λ 4772. With dilution the bands at λ 4737 and λ 4772 rapidly lose their identity, while the band whose center was at λ 4755 increases in intensity and somewhat asymmetrically, so that in the solution whose concentration was 0.99, with a depth of layer of 9 mm., there remains but a single band, its center being at λ 4760, and shading off towards both sides a little more than the corresponding band in the chloride solution. With increasing dilution this band also becomes more and more like the λ 4760 chloride band.

The chloride solution whose concentration was 1.7 normal, with a layer 3 mm. deep, showed a deep, narrow absorption band at λ 5090, and a wide, somewhat hazy one with its center at λ 5125. There was a region of transmission between the two about 15 A.U. wide. A, Plate 60, shows that these bands do not change materially with dilution to 0.22 normal.

The corresponding nitrate solution also shows a band at λ 5090, but it is much wider and hazier than in the chloride solution, while the λ 5125 band is, if anything, narrower. The two bands are not clearly separated in the first strip of B, Plate 70. With dilution, however, the λ 5090 band narrows up and becomes a little fainter, while the λ 5125 band widens a little towards the red; so that in rather dilute solutions the bands present the same appearance as they do in the corresponding chloride solutions. The region λ 5200 to λ 5240 shows practically continuous absorption with very hazy edges in the first strip of B, Plate 70 ; with dilution this changes rapidly, indicating bands somewhat similar to those of the chloride solutions belonging to A, Plate 60.

In A, Plate 71, the band has broken up, and instead of showing two narrow intense bands at λ 5205 and λ 5222 it shows the following : There is a deep, narrow band at λ 5205, a wider and very much more intense one at λ 5225, and a rather narrow, intense band at λ 5235. With increasing dilution the λ 5235 band diminishes in intensity, practically disappearing in the most dilute solution used in making B, Plate 71. At the same time λ 5225 decreases somewhat in intensity, and rather more on the red than on the violet side; so that when the most dilute solution of B, Plate 71, is reached its intensity is only slightly greater than that of the λ 5205 band and its center is at about λ 5222. Here, then, we find also the same general tendency for the spectrum of the nitrate solutions to change with dilution so as to become more and more like that of the chloride and bromide solutions.

We might go on and give in detail the changes taking place in the bands located in the yellow, orange, and red, since the changes here are just as well marked as those we have already described. But they all point to the same thing, namely, the dissimilarity of the spectra of concentrated solutions, and the gradual change of the nitrate spectrum into that of the chloride or bromide with decreasing concentration. That the spectra of dilute solutions should become more and more alike with increasing dilution was, of course, to be expected from the theory of dissociation; but on the simple theory of dissociation no one could have predicted that the chloride and bromide should give spectra which are practically identical, both in concentrated and in dilute solutions, while the nitrate should behave so differently, especially as it is well known that the three dry salts have quite different absorption spectra.

Our work on the spectrum of neodymium chloride in mixtures of alcohol and water made it seem very probable that the molecules as well as ions of the salt in solution are solvated, that is, have combined with them a relatively large number of molecules of the solvent. On this view, the results with aqueous solutions of the chloride, bromide, and nitrate are just about what we ought to expect, if we assume that the absorption bands are due to electrons which are located in or closely associated with the neodymium atom. Let us consider this a little more fully, even at the risk of repeating certain things we have said before.

Let the neodymium atom contain electrons, which if the atom is by itself would respond to light-waves of certain definite frequencies. White light, after having been acted on by a number of such atoms, would, when analyzed by a prism or grating, show a certain number of absorption bands whose wave-lengths could be determined. If, now, the atoms, instead of being free, are each united to 3 chlorine atoms, since these foreign atoms would affect the periods of the neodymium electrons, we should expect to find the absorption spectrum modified. If instead of 3 chlorine atoms we had united the neodymium atom with 3 bromine atoms, we should expect a somewhat different spectrum again, and so on for the various salts ; each one would be characterized by its own absorption spectrum. If these salts could be dissolved in some medium which had no action on it except to allow its molecules to move about freely, we should not expect any material change in the spectrum; while if the solvent united with it, forming solvates, we should expect the spectrum to be modified.

In a solvent like water, where it is probable that rather complex hydrates are formed, the *effect of the solvent might even become the most important factor in determining the character of the absorption.* To take a concrete case, suppose each molecule of a salt of neodymium in aqueous solution is united with 10 molecules of water. If the salt is the chloride or bromide, each neodymium atom has only 3 foreign atoms to disturb the periods of its electrons besides the 30 atoms in the combined water; while if the salt is the nitrate, it would have 12 foreign atoms besides those of the water. Evidently these 12 atoms would have a very much greater effect than the 3 in the case of the chloride or bromide, if we assume that the general arrangement in space is not very different in the two cases. We see, then, that the fact that the spectrum of the nitrate in aqueous solutions of considerable concentration is different from that of the chloride or bromide is what we should expect, and we also see that the very slight change in the spectrum of the bromide and chloride on dilution, as compared with the great change in case of the nitrate, might almost have been predicted.

The change taking place with dilution is, of course, due to dissociation, each neodymium atom after dissociation being simply united with, say, 10 molecules of water, the anion of the molecule having left it. The neodymium ions in dilute solutions are, therefore, the same, no matter what salt is in solution, if we assume that the presence of the anions in the solution does not influence the hydrating power of the metallic ion. Other things being equal, therefore, we should expect that salts whose molecules are made up of only a very few atoms united with a neodymium atom, in aqueous solution, should show the least change in the spectrum when the concentration is varied; since the removal of the few atoms making up the acid radical from the hydrated molecule would in general have but a slight effect on the periods of the absorbing electrons in the metallic atom. Salts whose molecules consist of a great many atoms united with a neodymium atom, like the nitrate, acetate, or sulphate, when dissolved in water, ought to show considerable change in their spectra as a result of dissociation, since the removal of the great number of atoms forming the acid radical would undoubtedly have a marked influence on the periods of the absorbing electrons.

It is plain, therefore, that the theory outlined above furnishes a perfectly simple and rational explanation of all the phenomena that have thus far been observed in the study of the absorption spectra of neodymium salts. That it also suffices for salts of the other rare earths studied will appear in what follows.

NEODYMIUM NITRATE IN WATER—MOLECULES CONSTANT. (See Plate 72 A.)

The concentrations of the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 1.34, 1.08, 0.79, 0.58, 0.43, 0.34, and 0.27; the corresponding depths of absorbing layer being 3, 4, 6, 9, 13, 18, and 24 mm.

As a rule the bands all widen and become somewhat more intense with increasing dilution, as might be expected from the spectrograms showing the behavior of the spectrum when the conditions for Beer's law obtain. The band at λ 4275, however, shows here the same change qualitatively as it did in the series for Beer's law; that is, the violet edge increases markedly in intensity. The red edge, however, remains of about the same intensity throughout, indicating that it owes its origin to the undissociated nitrate molecules.

The λ 4330 band, though rather faint, shows a considerable increase in intensity with dilution, again indicating that it is due to the same absorber that gives the violet edge of the λ 4275 band.

NEODYMIUM NITRATE IN METHYL ALCOHOL—BEER'S LAW. (See Plate 73.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.80, 0.64, 0.50, 0.40, 0.32, 0.25, and 0.20; and for B they were 0.32, 0.25, 0.20, 0.16, 0.13, 0.10, and 0.08; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. in both cases.

On account of the NO_3 band the spectrum terminates at λ 3250 in the ultra-violet for A, and at about λ 3200 for B.

The absorption near λ 3500 resembles that shown by aqueous solutions much more nearly than was the case with the chloride. Only two bands show, their positions being λ 3465 and λ 3545, respectively. The general shading extends from about λ 3450 to λ 3570.

The bands in the blue and violet are not as intense as the corresponding bands in the alcoholic solution of the chloride. Their positions and general character are much more nearly the same as those shown by concentrated solutions of the nitrate in water. There is a band at λ 4280, about 10 A.U. wide and not specially intense. At λ 4430 is a wide, faint band, and there is a similar one at λ 4600. Three faint bands show at λ 4690, λ 4735, and λ 4825, resembling very much the three corresponding bands in concentrated aqueous solution. The intensity here is, however, much less.

In the aqueous solution we found bands at λ 5205, λ 5225, and λ 5235, of which the first one was evidently due to the cation, the second one due partly to the cation and partly to the molecule, while the one at λ 5235 was apparently due only to the nitrate molecule. In the methyl alcohol solution, we find only a weak shade in the region λ 5200, while at λ 5225 and λ 5240 there are two rather narrow, intense bands. There is considerable shading to both sides of these bands.

In the yellow, A shows absorption from λ 5700 to λ 5870, shading off towards the red, with a band at λ 5965. B shows a band at λ 5720, which is perhaps double; deep absorption from λ 5755 to λ 5845, with faint bands at λ 5760 and λ 5835, and a very intense band at λ 5790.

The spectrum ends near λ 7320 in a band, which does not seem especially intense.

NEODYMIUM NITRATE IN ETHYL ALCOHOL—BEER'S LAW. (See Plate 74.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.32, 0.26, 0.20, 0.16, 0.13, 0.10, and 0.08, and for B they were in the same order, 0.16, 0.13, 0.10, 0.08, 0.06, 0.05, and 0.04; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm.

The solutions used in making A of this plate had the same concentrations as those used in making B of Plate 73, and as the depths of absorbing layer were also the same, the two plates are directly comparable.

The two spectra are very similar, but nevertheless there are some well-marked differences. The bands at λ 5225 and λ 5240, which were quite sharp and intense in the methyl alcohol solution, here show simply as one hazy band of moderate intensity, its middle being near λ 5235. Even in B, where the concentration is much less, this band does not break up into two, but simply diminishes in intensity without change of character.

The yellow group shows a wide, faint band at λ 5730, a moderately intense band at about λ 5790, much less intense and sharp than in methyl alcohol. There is a pair of poorly defined bands at λ 5825 and λ 5845, apparently corresponding to the band at λ 5835, observed in the solutions in methyl alcohol.

The spectrum ends at λ 7315 in a band which is not very intense or sharp. In general, the absorption in the two alcohols is about the same, the tendency being for all absorption bands to be narrower in the methyl alcohol than in the ethyl alcohol solutions.

NEODYMIUM NITRATE IN ACETONE—BEER'S LAW. (See Plate 75.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.60, 0.48, 0.37, 0.30, 0.24, 0.19, and 0.15. For B they were 0.19, 0.15, 0.12, 0.095, 0.075, 0.060, and 0.047; the depths of absorbing layer were in both cases 6, 7.5, 9.5, 12, 15, 19, and 24 mm.

The nitrate was found to be much more soluble in acetone than in ethyl alcohol, being in this respect quite different from the chloride, which, when anhydrous, dissolves quite readily in ethyl alcohol, but scarcely at all in acetone.

The spectrum in the ultra-violet ends at about λ 3300, as is usual in acetone solutions. The bands in the ultra-violet absorption near λ 3500 have the positions λ 3475 and λ 3555, are both rather faint, and have a width of about 15 or 20 A.U. They are hence both wider and fainter than they were in the methyl alcohol solution. Their position is apparently about 10 A.U. nearer the red end of the spectrum than was the case in the alcoholic solutions, but the greater part of this is perhaps due to the broadening, which is somewhat unsymmetrical.

The band at λ 4280 is about 15 A.U. wide and not very intense. The other bands in the violet, blue, and blue-green are so faint as to make measurements impossible. Apparently they agree pretty well in general appearance and position with the corresponding bands in methyl alcohol. However, much deeper layers of the solution than could possibly be used with the apparatus employed in the present investigation would be needed in order to study these bands at all carefully.

At λ 5110 there is a fairly intense, but wide and hazy band. λ 5215 is another similar in appearance to the one at λ 5110, though not quite as hazy. It is not entirely separated from the much more intense band at λ 5255. The latter corresponds to the doublet λ 5225 and λ 5240 in methyl alcohol, and the hazy band at about λ 5235 in ethyl alcohol. Its position is therefore somewhat nearer the red end of the spectrum.

In the yellow A shows absorption from λ 5690 to λ 5900. At λ 6020 is a moderately intense but rather wide band, which has a fainter and narrower companion at λ 6040.

There is a set of bands in the region λ 6100 to λ 6300, which seems to increase somewhat in intensity towards the red; but the absorption is too faint to allow the individual bands to be picked out. There is a moderately intense but hazy band at λ 6760. The spectrum ends near λ 7300. B shows the yellow group broken up into two moderately intense but rather wide bands at λ 5725 and λ 5775, and a much wider and stronger band, with its center at λ 5840, which is strongly shaded to both sides. Indications are that this band is at least double, the more intense component being towards the violet. The spectrum shown in B ends at λ 7315, and there is a slight indication that between this point and λ 7400 there is a group of three or more bands.

In general, it appears that as the molecular weight of the solvent is increased the absorption bands become wider and wider. In aqueous solutions there are a number of bands having a width of only a few Ångström units, while in methyl alcohol few bands are narrower than from 8 to 12 units. In ethyl alcohol no band is narrower than 10 to 15 units, and in the acetone their width is still greater.

NEODYMIUM NITRATE IN MIXTURES OF METHYL ALCOHOL AND WATER.

(See Plate 76 A.)

The concentration of the neodymium nitrate was constant throughout and equal to 0.5 normal. The percentages of water in the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0, 16.6, 33.3, 50, 66.6, 83.3, and 100 per cent. The common depth of absorbing layer was 0.5 cm.

The changes here are similar to those discussed in considering Plate 65; that is, the change from the bands characteristic of the aqueous solution to those belonging to the alcoholic solution takes place in passing from the solution containing 16.6 per cent of water to the one containing no water. The spectrogram, however, shows that the spectrum changes considerably from solution to solution, even when the percentage of water is much greater; for example, changes may be noticed in passing from the solution containing 100 per cent water to the one containing 50 per cent. This is undoubtedly due to the change in the dissociation of the dissolved salt, which, in the case of the nitrate, modifies the spectrum; while in the case of the chloride no such change was noted, except at the very greatest concentrations. The spectrogram, therefore, shows a superposition of the two effects, and if this is borne in mind everything about it is perfectly clear without further discussion.

NEODYMIUM NITRATE IN MIXTURES OF ACETONE AND WATER. (See Plate 67 B.)

The concentration of the neodymium nitrate was constant throughout and equal to 0.6 normal. The percentages of water in the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0, 2.6, 5.3, 8, 10.6, 13.3, and 16. The common depth of absorbing layer for all the solutions was 0.5 cm.

In this, as well as in the case treated under Plate 76 A, we have to do with a superposition of two effects. First, the change produced in the water solution resulting from decreased dissociation with the addition of the non-aqueous solvent; and secondly, the change in the structure of the bands which takes place when the amount of water has been decreased so far that the molecules of the dissolved substance are no longer able to be surrounded by the usual number of water-molecules, but become surrounded by molecules of the non-aqueous solvent—in the present case acetone. In the solution whose spectrum is nearest the narrow, comparison spark spectrum, the percentage of water being only 16 per cent, the dissociation is already rather slight, so that the spectrum is approximately that which we would observe in a very concentrated aqueous solution of the salt in a layer only about a millimeter in depth. With decrease in the amount of water the change is easiest to follow in the more intense of the bands in the green, this being the one which differs most in the acetone and concentrated aqueous solutions. It will be noticed that the most marked change in this band takes place in passing from the fifth to the third strips, counting from the scale; that is, when the water content of the solvent changes from 10.6 to 5.3 per cent. This agrees substantially with what we found to hold in the case of solutions of the chloride in mixtures of water and the alcohols.

PRASEODYMIUM CHLORIDE IN WATER—BEER'S LAW. (See Plate 77.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.56, 1.92, 1.28, 0.85, 0.60, 0.42, and 0.32. For B the concentrations were 0.85, 0.63, 0.42, 0.28, 0.20, 0.14, and 0.11, the depths of absorbing layer being respectively 3, 4, 6, 9, 13, 18, and 24 mm.

The solutions of praseodymium chloride are all green or yellowish-green, only the intensity of the color changing with change in the concentration.

For these solutions Beer's law holds very exactly, excepting for the extreme ultra-violet absorption in A, and the yellow bands in the two or three most concentrated solutions of A.

The limits of transmission in the ultra-violet, for the most concentrated and most dilute solutions of A, are, respectively, λ 2720 and λ 2650. The edge is fairly sharp, indicating the presence of a rather intense band. This is also indicated by B, where the spectrum ends abruptly at λ 2630, the limit being the same for all of the solutions.

The absorption bands shown in A are as follows: λ 4380 to λ 4480, strong band with red edge somewhat shaded; λ 4640 to λ 4710, sharp on red side, quite diffuse towards the violet; λ 4800 to λ 4830, sharply defined on both sides; λ 5860 to λ 5950, both edges diffuse; λ 5985, fairly narrow band with diffuse edges. The region between this band and the principal yellow one shows very strong absorption.

B shows the following: λ 4410 to λ 4465, both edges a little diffuse; λ 4685, fairly narrow band, still more diffuse towards the violet, although somewhat shaded also towards the red; λ 4815, narrow band, with edges slightly shaded; λ 5900, wide hazy band; absorption not complete, even at its middle; λ 5985, rather faint, hazy band.

The greenish tinge of the solutions would suggest that there is considerable general absorption in the red, because the absorption in the yellow is not sufficient to impart any marked color to the solution, and the bands in the violet and blue could only give it a yellow tint. The negative for A does, in fact, show pretty strong general absorption from λ 7100 to the end of the red, but no doubt a spectrophotometric study of the solutions would show general absorption much farther down into the red. The negative for B shows no sign of this absorption, for very obvious reasons.

Praseodymium Chloride in Mixtures of the Alcohols and Water.
(See Plate 78.)

The concentration of the praseodymium chloride was constant throughout and equal to 0.5 normal. The percentages of water in the solutions, beginning with the one whose spectrum is adjacent to the numbered scale, were 0, 2.3, 5.6, 8, 10.6, 13.3, and 16. The depth of absorbing layer was 1.0 cm. Methyl alcohol was the chief solvent in the solutions pertaining to A, while ethyl alcohol was employed in the solutions used in making the negative for B. The two spectrograms are identical, except for a little greater general absorption in the ultra-violet with the ethyl alcohol. The most striking feature of the spectrograms is the appearance of the intense absorption band near λ 3000 as the percentage of water is gradually decreased. Only a faint trace of this band is visible with 16 per cent of water in the solution, and the band is comparatively weak even with only 8 per cent of water. From this point it increases very rapidly in width and intensity with decrease in the amount of water, until in the pure alcohol solutions its limits (transmission) are λ 2970 and λ 3230, being by far the most intense band in the whole spectrum.

The bands in the violet and blue apparently shift somewhat towards the red, this being, however, due to the fact that the alcohol bands are a little nearer the red end of the spectrum, and that when the percentage of water changes from 16 to 0, the two sets of bands coexist, but are far from being separated. The change is exactly the same in character as the one described in detail in discussing the λ 4760 band for neodymium chloride in mixtures of alcohol and water.

The positions of the bands in the solution containing 16 per cent of water are as follows : λ 4390 to λ 4470, λ 4660 to λ 4700, λ 4800 to λ 4825. In the solution in pure alcohol they are λ 4410 to λ 4480, λ 4690 to λ 4715, λ 4810 to λ 4840. Hence, it appears that the two most refrangible bands have a slightly greater width in the water solution, while the λ 4815 band is more intense in the alcoholic solutions.

The bands in the yellow show very well indeed the fact that here as in the spectrum of neodymium chloride we have the coexistence of two sets of bands when the water content of a 0.5 normal solution is in the neighborhood of 8 per cent. The band in the yellow has already been described under Beer's law, but as the concentration and depth of layer are different here, the following will serve to indicate what the spectrum of the 16 per cent water solution shows. Absorption begins at λ 5850 and rises to a maximum at about λ 5900, then decreases to a minimum at λ 5950, from which it again rises to a maximum at about λ 5980, falling off to zero at λ 6000. The solution in pure alcohol shows the following : Weak absorption begins at λ 5800 and continues without material change up to λ 5880, where it falls almost to nothing. At λ 5900 it begins to increase and reaches a strong maximum at λ 5955, falling off gradually to zero at λ 6000. The intermediate solutions show the gradual disappearance of the bands characteristic of the aqueous solution, and the increase in intensity of those belonging to the alcoholic solution, as the percentage of water is gradually decreased. The maximum change takes place from the fifth to the third strips, counting from the numbered scale, indicating here, as with neodymium chloride, that the two sets have about half their normal intensity when the water content of the solution is about 8 per cent, or when the solution contains about 10 molecules of water per molecule of the dissolved substance.

PRASEODYMIUM NITRATE IN WATER—BEER'S LAW. (See Plate 79.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 3.2, 2.4, 1.6, 1.1, 0.75, 0.53, and 0.41. For B the concentrations were 1.1, 0.80, 0.55, 0.33, 0.26, 0.18, and 0.14; the depths of absorbing layer in both cases were 3, 4, 6, 9, 13, 18, and 24 mm.

There is a great deal of absorption in the ultra-violet, the spectrum of the most concentrated solution ending at λ 4000, while that of the four most dilute solutions of set A ends at about λ 3650. The spectra shown in B all end at λ 3570. This absorption is not to be ascribed to the NO_3 radical, as its band lies beyond λ 3300 in all the solutions thus far studied.

The absorption bands do not differ materially from those of the chloride, except that they are a trifle more intense, due, no doubt, to the slightly greater concentration of the nitrate solutions. Also, the violet and blue bands show a slight deviation from Beer's law in the two or three most concentrated solutions of A.

ERBIUM CHLORIDE IN WATER—BEER'S LAW. (See Plate 80.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 1.4, 1.18, 0.98, 0.80, 0.66, 0.56, and 0.47. The concentrations for B were 0.80, 0.67, 0.56, 0.46, 0.38, 0.32, and 0.27, the corresponding depths of absorbing layer being 8, 9.5, 11.5, 14, 17, and 24 mm.

The concentrations here given were obtained by assuming the atomic weight of the metallic atom as 166, that is, assuming that the solution was one of pure erbium chloride. As the salt contained very large quantities of yttrium and other related elements, the figures given for the concentration can have no meaning in the absolute sense. They merely indicate the *relative* amounts of erbium chloride in the different solutions employed.

For these solutions of the chloride Beer's law holds pretty accurately, excepting for the absorption in the extreme ultra-violet, where the limits of transmission for the most concentrated and most dilute solutions of A are λ 2870 and λ 2760. For B the corresponding figures are λ 2760 and λ 2650.

The positions of the chief bands are as follows: λ 3240, λ 3500, λ 3635, and λ 3785 in the region covered by the spark spectrum; λ 4150, λ 4210, λ 4415, λ 4495 moderately strong, λ 4515 fairly intense, λ 4670 very faint, λ 4845, λ 4865 intense, λ 4905, λ 5185 faint, λ 5205 fairly intense, λ 5230 intense, λ 5365, λ 5415, λ 5435, λ 5490 faint, λ 6410 faint, λ 6490 faint, λ 6535 fairly intense, and λ 6680 rather faint.

ERBIUM NITRATE IN WATER—BEER'S LAW. (See Plate 81.)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 1.4, 1.05, 0.88, 0.70, 0.56, 0.44, and 0.35. For B the concentrations were 0.70, 0.52, 0.44, 0.35, 0.28, 0.22, and 0.17, the depths of absorbing layer being in both cases 6, 7.5, 9.5, 12, 15, 19, and 24 mm.

What was said about the significance of the figures given for the concentrations under erbium chloride, applies equally well in this case, since the same material was used. Here the ultra-violet is limited by the NO_3 band at about λ 3300 as usual.

The more concentrated solutions give a spectrum which is somewhat different from that produced by the chloride solutions. The bands are as a rule wider and hazier, and their intensity maxima sometimes fall in slightly different positions. With dilution the character of the bands changes considerably, becoming more and more like the bands given by the chloride solution. Here, again, then, we find a state of affairs very like the one we discussed at some length under neodymium nitrate—Beer's law.

Judging from the negatives made with the solutions of erbium salts, it appears that the absorption spectrum of erbium would make fully as interesting a study as that of neodymium, and it is to be hoped that in the continuation of this work some preparation richer in erbium than the one we employed will be available.

It may be said in general that the absorption spectra of the different salts of the same metal resemble each other very closely; and it is only when careful attention is paid to the structure of each individual band, or group of bands, that the differences are brought out clearly. In the process of printing and reproducing the spectrograms illustrating this chapter, a great deal of the finer detail has been lost, and as it is just this detail which shows the differences alluded to above, it is clear that in many cases the reproductions fail entirely to show the important points. In cases of special importance a rather full description of the appearance as seen on the negatives has been given in the text. A full description of this nature covering all the spectrograms of the present chapter would require an amount of time and space that would be quite prohibitive, and unnecessary.

It is hoped, however, that the plates, together with the description given in the text, will make clear the points which we have tried to emphasize most strongly, viz:

1. That the absorption spectra of different salts of the same metal in the same solvent are different if the concentration is great, or, more generally, if the dissociation is only slight; and that as the dissociation becomes more and more complete, they become more and more alike.

2. That the absorption spectra of the same salt in different solvents are in general different.

3. That with change in dissociation of the salt in any one solvent, the change in the absorption spectrum of salts having anions containing only a few atoms, such as the chloride and bromide, is very slight; but that as the complexity of the anion increases, the change becomes more and more pronounced.

4. That when a salt is dissolved in mixtures of two solvents, the relative percentages of which are varied, there is not a gradual change of one spectrum into the other; but the spectrum given by the mixture is a superposition of the two spectra, the two sets of bands existing together. If the salt is one whose spectrum changes considerably with its state of dissociation, we have in addition to the above phenomena the changes due to the varying dissociation of the dissolved salt produced by the varying composition of the mixture.

The explanation of these points on the working hypothesis which has guided the present work, has already been given in the discussion of Plates 70 and 71.

In the introduction to the present chapter the work of Helen Schaeffer was referred to. It will be recalled that she studied the spectrum of the nitrate of neodymium in various solvents, and also in mixtures of two solvents; the case to which she calls special attention being mixtures in various proportions of water and acetone. She did not come to the conclusion which we have reached, that in such mixtures we have two distinct sets of absorption bands, since she considers the bands as shifting gradually, some in the direction demanded by Kundt's law, and some in the opposite direction. There are two reasons why she did not come to the same conclusion that we have reached. In the first place she worked with the nitrate, which we have found shows a considerable variation in its spectrum with change in dissociation, and her solvents being water and acetone, the change in the dissociation would be very considerable. For this reason, she found a continuous change in the spectrum as more and more acetone was added, which was just what she expected. Had she worked with the chloride or bromide she would have found practically no change until the proportion of the non-aqueous solvent in the mixture had become very great, and in this event her conclusions would have been quite different.

In the second case her salts were not dehydrated (if they were she makes no mention of the fact), and hence even in the solution in pure acetone she probably had from 6 to 10 molecules of water per molecule of the dissolved salt, which we have found would give the spectrum characteristic of the non-aqueous solvent with only about half its normal intensity. It is not very surprising, therefore, that she failed to discover the coexistence of the two sets of bands, which would have given a perfectly simple explanation of all the phenomena that she observed.

CHAPTER VIII.

SUMMARY AND CONCLUSIONS.

It is evident from the spectra of the solutions studied in the present investigation that deviation from Beer's law is the rule rather than the exception. Of the great number of sets of solutions studied, only a very limited number appear to confirm Beer's law, and it is possible that with the more exact spectrophotometric measurements this number would be reduced still further. This is exactly what we should expect, since actual solutions always contain more than one kind of "absorber," and the relative concentrations of these "absorbers" are continually changing with change in concentration of the solution. Beer's law could only hold, as explained in the introductory chapter, in cases where the relative concentrations of the different kinds of absorbers do not change with dilution, or in the event that the absorption of all the different kinds of absorbers is identical. The first one of these conditions is perhaps never fulfilled, while the second one is undoubtedly approached more or less closely in certain cases, such as in aqueous solutions of neodymium chloride or bromide or of praseodymium chloride. The rule is, however, that the different absorbers have different absorbing powers, and the problem is, therefore, to decide which absorbers are responsible for the bands observed in the various spectra.

According to the theory of Ostwald, which is simply Arrhenius's dissociation theory applied to the absorption spectra of solutions, we have but two or three kinds of absorbers, namely, the molecules of the dissolved salt and one or both the ions formed from it. In the case of all the salts studied in the present work, excepting the nitrates, the anion has been colorless; so all the absorption, according to Ostwald's theory, should be due to two kinds of absorbers, the molecule and the cation. That this theory fails entirely to account for the deviation from Beer's law observed in the ultra-violet absorption of copper salts, the red bands of cobalt salts, the ultra-violet band of cobalt chloride, and the absorption of iron chloride, has already been pointed out; since all of these bands narrow with dilution, even when the number of molecules in the path of the beam of light is kept constant. Whether this theory is able to account for the behavior of those bands which narrow with dilution when the conditions for Beer's law obtain, but which widen when molecules are kept constant, can only be decided by spectrophotometric measurements.

The work of Müller on salts of nickel and copper shows that the behavior of the red absorption band of these substances can not be accounted for on Ostwald's theory, and this makes it at least very probable that the same will be found for salts of other metals. Ostwald's theory may, therefore, be dismissed, not because it is erroneous, but because it is incomplete. It leaves out of account certain changes taking place in solutions, which produce other "absorbers" than those which it considers.

The other theories which aim to account for the deviations are of two kinds, viz:

(1) Those that assume that the increased absorption in concentrated solutions is due to the formation of aggregates of the molecules of the dissolved substance, or of the molecules and the ions into which they break down on dissociation.

(2) Those that assume that the deviation is due to the formation of solvates, that is, combinations of the parts of the dissolved substance with the molecules of the solvent.

It has been shown by Hartley and other workers who have studied the change in the absorption with change in temperature, that the bands which widen with increase in concentration (conditions for Beer's law assumed to obtain) also widen with rise in temperature; that is, a rise in temperature produces very much the same effect as increase in concentration. This seems to us pretty conclusive evidence against the theories that are based on the formation of aggregates, for it is well known that the change in the aggregates produced by rise in temperature is *not the same* as that produced by increase in concentration, but *exactly the opposite.*

The theories which assume the formation of solvates are not open to this objection, because it is well known that the change in the solvates produced by rise in temperature is in general the *same* as that produced by increase in concentration. As a solution becomes more concentrated the solvates become simpler and simpler, that is, fewer molecules of the solvent are combined with each part of the dissolved substance. Rise in temperature also breaks down complex solvates into simpler ones. Of course, it does not follow that the solvates of a solution of concentration c_1 at temperature t_1 are *exactly* the same as those in a solution of concentration c_2 at a temperature t_2; since under the changed conditions it may happen that the particular solvates which were most stable when the conditions were c_1 and t_1 may be less stable than solvates of nearly the same composition at c_2, t_2.

For this reason, and also because *our work on neodymium and praseodymium salts in mixed solvates seems almost conclusive evidence in favor of the existence of solvates,* we have used the solvate theory as a working hypothesis throughout this investigation. That it is not far from being correct is shown by the fact that all the phenomena observed in the great number of solutions studied are accounted for without anything but the simplest assumptions in regard to the behavior of the solvates in question.

We shall now summarize briefly the main points brought out in the present work.

Solutions of cobalt salts have, in general, three regions of absorption in that part of the spectrum which can be photographed without resorting to other means than the commercial dry plate. One is in the extreme ultra-violet, and we concluded that it is due to the molecules of the dissolved substance. Their absorption is influenced to some slight extent by solvation, but differently for the different salts. That no part of this absorption is due to the cobalt ions is shown by the fact that solutions of cobalt sulphate are perfectly transparent beyond λ 2200, although they are dissociated to a very considerable extent.

Another region of absorption is in the green, near λ 5200, for most solutions. This band, which is the most characteristic one of cobalt solutions, was ascribed by Ostwald to the cobalt ion. That the molecules also absorb in this region, and in fact have a greater absorbing power than the ion, has been abundantly shown in Chapter II. Whether the simple theory of dissociation is able to account for the observed deviations from Beer's law for this band is not known, but is improbable. The question is now being investigated in this laboratory, and a definite answer will probably be given in the near future.

The absorption band at λ 3300 in the spectrum of the aqueous solution of cobalt chloride, since it disappears with dilution even when molecules are kept constant, can not be due to the cobalt chloride molecules; but we found good reasons for thinking that it is due to some hydrate of these molecules which is formed in solutions of moderate concentration even at ordinary temperature. The two bands in the same region, which appear in the alcoholic solutions of the same salt, behave so much like the band in the aqueous solution that they are undoubtedly due to some relatively simple alcoholate.

The bands in the red region of the spectrum of solutions of cobalt salts we concluded were due to very simple solvates, such as are formed only in the most concentrated aqueous solutions, or in such solutions of moderate concentration, but at very high temperatures. Donnan and Bassett assumed that these bands are due to some complex anions, such as $CoCl_2.Cl$ or $CoCl_2.Cl_2$, which would then be the same in aqueous and non-aqueous solutions. There are a great many objections to this explanation. In the first place, such complexes ought to obey the usual rule for aggregates, that is, they ought to break down with rise in temperature, whereas the change in the spectrum demands the opposite. In the second place, according to this theory, the bands ought probably to be the same in aqueous as in non-aqueous solutions, which we have found is not the case. *On the theory of solvates, however, everything is perfectly clear.* The difference in the structure of the group of bands with different solvents is what we should expect, and the appearance of the bands with rise in temperature of aqueous solutions, or with the addition of large quantities of a dehydrating agent, is simply due to the formation of the required simple hydrates under these conditions.

The bands of solutions of nickel salts are all of the same type as the green cobalt band, and hence must be studied spectrophotometrically. The change in the ultra-violet band with addition of dehydrating agents, however, suggests that here also hydrates play an important part. Anhydrous nickel chloride could not be dissolved in the non-aqueous solvents used, hence the work was of necessity limited to aqueous solutions.

With the exception of copper chloride in acetone, which has a band at λ 4700, all copper solutions show only two regions of absorption, one in the ultra-violet and one in the red. The ultra-violet band, since it narrows rapidly with dilution even when molecules are kept constant, can not be accounted for by the simple theory of dissociation. And as it widens rapidly with rise in temperature, we must conclude that it is due to the solvated molecules, the absorbing power of which increases rapidly with decrease in the complexity of the solvate.

The band in the red belongs in the same class with the green cobalt band. But, as mentioned above, Müller came to the conclusion that dissociation is unable to account for its deviation from Beer's law, which also agrees with what we found in studying its behavior in mixtures of alcohol and water for the case of the chloride. Hence we assume that solvates here also play a rôle, which, however, is not quite so apparent, owing to the fact that both the solvated ions and the molecules absorb light in this region.

Another fact which supports our view is that the absorption in the red is not widely different in different solvents, provided the concentrations are about the same; while in the ultra-violet the absorption is many times greater in the non-aqueous than in the aqueous solvents; the reason for the latter being, first, that the dissociation in aqueous solutions is much greater than in non-aqueous, and hence, for equal concentrations, the number of molecules in the latter is much greater than in the former. Secondly, the solvating power of water is much greater than that of the non-aqueous solvents used, and hence the comparatively few molecules present, by forming relatively complex hydrates, have their absorbing power still further reduced.

The only salt of iron studied was ferric chloride. It shows only one region of absorption, namely, the one which cuts off the entire ultra-violet, and usually also the violet and blue portion of the spectrum. In aqueous solutions this absorption band narrows very rapidly with dilution, even when molecules are kept constant, indicating a marked effect of hydration. In alcoholic solutions the band remains of sensibly constant width, indicating that in this case the solvation is probably very slight. The difficulty in drawing any definite conclusions from solutions of this salt is that the solutions are not very stable, and hence the effects may very often be marked by chemical changes of unknown amount.

Chromium salts behave very much like those of nickel. Only two of them were studied in this work and these only in aqueous solution. The behavior of their bands is quite analogous to that of the green cobalt band, and hence calls for spectrophotometric study. Their diffuse character also makes them rather unfit for spectrographic investigations.

The most interesting and important results were obtained from the study of the salts of neodymium and praseodymium, especially those of the former. These substances have not only very many absorption bands, but they are remarkably narrow and sharp, and hence peculiarly suitable for spectrographic study.

The chief experimental results were the following:

1. The absorption spectrum of aqueous solutions of the chloride and bromide of neodymium changes very little with change in concentration, and the two are nearly identical throughout, excepting for the fact that the absorbing power of the bromide appears to be somewhat greater than that of the chloride.

2. The absorption spectrum of aqueous solutions of neodymium nitrate is somewhat different from that of the chloride or bromide, especially if

the solutions are concentrated. With decrease in concentration the spectrum changes so as to become more and more nearly identical with that of the other salts. Certain bands, therefore, increase in intensity when the conditions for Beer's law obtain. Others decrease and only remain constant when molecules are kept constant. Examples of the first class of bands are those at λ 4275, λ 4330, and λ 5205. Examples of the second kind are the bands at λ 4282 and λ 5235.

3. Addition of large amounts of calcium or aluminium chloride to a solution of neodymium chloride does not affect the spectrum appreciably, except the shading of the yellow band, and perhaps very slightly that of the green bands.

4. Solutions of the salts in non-aqueous solvents give spectra which are not only different for different salts, but the spectrum of any one salt is different in the different solvents. An apparent exception is the spectrum of neodymium or praseodymium chloride in methyl and ethyl alcohols, which are almost exactly alike.

5. When a salt like neodymium chloride is dissolved in mixtures of water and one of the non-aqueous solvents, and the relative amount of the two solvents in the mixture is varied, no marked change in the spectrum is observed when the amount of water is changed from 100 per cent to about 15 or 20 per cent. As the amount of water is still further reduced, we find that the solution gives a spectrum which consists of a superposition of the spectra belonging to the aqueous and the non-aqueous solutions, the former decreasing in intensity while the latter increases as the amount of water is decreased. The composition of the mixed solvent which will show the two spectra with about half their normal intensity, depends upon the concentration of the salt in solution, and a constant ratio between the number of molecules of water and those of the dissolved salt was indicated by the experiments; this ratio having the value 10.

Neodymium nitrate dissolved in mixtures of water and one of the non-aqueous solvents shows exactly the same change as the chloride; but in addition we get the changes in the spectrum produced by the great change in the state of dissociation of the salt. The result is that the whole change is a much more gradual one, and hence is not nearly so striking as it is in the chloride or bromide solutions.

Praseodymium chloride dissolved in mixtures of water and methyl or ethyl alcohol shows, in general, the same kind of change in the spectrum as neodymium chloride, but in addition there appears in the alcoholic solutions an entirely new band having no analogue in the aqueous solution. In the former this new band in the ultra-violet is by far the most intense in the entire spectrum. It disappears entirely by addition of water, having about half its normal intensity for a half-normal solution when the water content of the solvent is about 8 per cent.

These facts seem to us inexplicable on any other hypothesis than the one we have advanced, namely, that when a salt of one of these elements is dissolved in a solvent both the molecules of the salt and the ions formed from them become solvated, that is, they combine with a certain number of molecules of the solvent. In the case of cobalt and copper salts we found reasons for believing that a series of solvates of varying complexity was formed, while with these rare elements the spectrum rather points to the existence of only one definite solvate. A more extended study, including the changes in the spectrum produced by change in temperature, may, however, modify this conclusion somewhat.

Granting the existence of the solvates, the phenomena observed in the absorption spectra of neodymium and praseodymium admit of a perfectly natural explanation. As this explanation has already been given in full under the discussion of neodymium nitrate in water—Beer's law—we need not repeat any part of it.

INDEX.

Absorption and solvation..............101
spectra of solutions......... 1
theories of absorption......101
Acetone and water, neodymium nitrate in mixtures of..................... 94
Acetone, cobalt bromide in—Beer's law. 26
chloride in—Beer's law. 18
copper chloride in—Beer's law. 48
with water 50
ferric chloride in—Beer's law. 62
neodymium nitrate in—Beer's law....................... 92
with water, cobalt bromide in. 28
chloride in. 21
Alcohols and water, praseodymium chloride in mixtures of the.......... 95
Aluminium and calcium chlorides—
with chromium chloride........... 65
with neodymium chloride in water. 77
with nickel chloride in water...... 41
Aluminium chloride with ferric chloride. 60
Ames, J. S.......................Preface
Anderson, on the absorption spectra of dry neodymium salts...... 85
on the absorption spectra of powdered salts of neodymium and erbium 71
Anhydrous neodymium chloride........ 84
salts, preparation of........ 71
Apparatus.......................... 6
Association......................... 2

Babo, work on cobalt salts............. 11
Bahr and Bunsen, on the absorption spectra of compounds of didymium... 68
Bassett and Donnan 5
assume complex ions.............. 35
on the absorption of cobalt salts...102
on the absorption spectra of copper salts.......................... 45
on the color changes in cobalt salts. 13
Becquerel, absorption spectra of chromium compounds......... 63
on the absorption spectra of didymium compounds..68, 70
on the absorption spectra of neodymium salts......... 85
Beer's law.......................... 1
Beer's law for—
chromium chloride in water....... 64
nitrate in water........ 66
cobalt bromide in ethyl alcohol.... 25
in methyl alcohol.. 25
in water........... 22
chloride in acetone.......... 18
in ethyl alcohol.... 17
in methyl alcohol.. 16
Beer's law for—
cobalt chloride in water........... 13
sulphate in water........... 31
sulphocyanate in water...32, 34
copper bromide in ethyl alcohol.... 53
in methyl alcohol... 52
in water........... 51
chloride in acetone 48
in ethyl alcohol 47
in methyl alcohol... 46
in water 45
nitrate in water 55
erbium chloride in water........... 97
nitrate in water........... 97
ferric chloride in acetone......... 62
in ethyl alcohol 61
in methyl alcohol.. 61
in water 59
neodymium bromide in water...... 86
chloride in ethyl alcohol 78
chloride in methyl alcohol 77
chloride in water 72
nitrate in acetone.... 92
nitrate in ethyl alcohol 92
nitrate in methyl alcohol 91
nitrate in water...... 87
nickel acetate in water............ 43
chloride in water........... 39
sulphate in water........... 42
praseodymium chloride in water... 94
nitrate in water.... 96
Bersch, work on cobalt salts 11
Bettendorff, on the absorption spectra of the rare earths 68
Boudouard, on the absorption spectra of praseodymium and neodymium...... 68
Brewster, absorption spectra of chromium salts............... 63
on the absorption spectrum of nickel nitrate............. 39
Bunsen and Bahr, on the absorption spectra of didymium compounds..... 68
Bunsen, on the absorption spectra of didymium salts..................... 70

Calcium and aluminium chlorides—
with chromium chloride........... 65
with neodymium chloride in water. 77
with nickel chloride in water....... 41
Calcium bromide with cobalt bromide.. 23
chloride with ferric chloride.... 60
Chatelier, Le, on the color changes in cobalt salts........................ 12

Chromium chloride in water—Beer's law. 64
  in water—molecules constant 65
  with calcium and aluminium chlorides . 65
Chromium nitrate in water—Beer's law. 66
  in water—molecules constant.......... 67
Chromium, salts of.................... 63
Cobalt acetate in water—Beer's law.... 34
Cobalt bromide in—
  acetone—Beer's law............... 26
    with water.............. 28
  ethyl alcohol—Beer's law.......... 25
    with water......... 27
  methyl alcohol—Beer's law........ 25
    with water....... 27
  water—Beer's law................ 22
    molecules constant......... 22
Cobalt bromide with calcium bromide.. 23
Cobalt chloride in—
  acetone—Beer's law............... 18
  acetone with water................ 21
  ethyl alcohol—Beer's law......... 17
  ethyl alcohol with water........... 20
  methyl alcohol—Beer's law........ 16
  methyl alcohol with water......... 19
  water—Beer's law.... 13
  water—ions constant.............. 15
  water—molecules constant........ 15
Cobalt nitrate in water—molecules constant............................ 30
Cobalt, salts of...................... 11
  salts, summary of results with... 35
  sulphate in water—Beer's law... 31
  sulphocyanate in water—Beer's law......................... 32
  sulphocyanate in water—molecules constant................ 33
Conclusions and summary.............100
Copper bromide in—
  ethyl alcohol and water........... 54
    —Beer's law......... 53
  methyl alcohol and water..... ... 54
    —Beer's law 52
  water—Beer's law................ 51
    molecules constant......... 52
Copper chloride in—
  acetone—Beer's law 48
    with water.............. 50
  ethyl alcohol—Beer's law.......... 47
    with water......... 50
  methyl alcohol—Beer's law........ 46
    with water....... 49
  water—Beer's law................ 45
    molecules constant........ 46
Copper nitrate in water—Beer's law.... 55
  in water—molecules constant................ 56
Copper, salts of...................... 45
Croft, absorption spectra of chromium compounds........................ 63

Demarçay, on the absorption spectra of didymium compounds............... 68
Dissociation.......................... 2
Donnan and Bassett.................. 5
  assume complex ions.............. 35
  on the absorption of cobalt salts....102
  on the absorption spectra of copper salts.......................... 45
  on the color changes in cobalt salts. 13
Drossbach, absorption spectra of praseodymium and neodymium compounds. 70

Emsmann, on the absorption spectrum of nickel nitrate.................... 39
Engel, on the color changes in cobalt salts 11
Erbium chloride in water—Beer's law.. 97
  nitrate in water—Beer's law... 97
  salts of...................... 68
Etard, on the absorption spectra of chromium compounds....... 64
  on the color changes and solubility of cobalt salts......... 11
Ethyl alcohol—
  and water, copper bromide in...... 54
  and water, neodymium chloride in. 83
  cobalt bromide in—Beer's law..... 25
  cobalt chloride in—Beer's law..... 17
  copper bromide in—Beer's law.... 53
  copper chloride in—Beer's law..... 47
  ferric chloride in—Beer's law...... 61
  neodymium chloride in—Beer's law 78
  neodymium nitrate in—Beer's law. 92
  with water—cobalt bromide in..... 27
  with water—cobalt chloride in..... 20
  with water—copper chloride in..... 50

Ferric chloride—
  in acetone—Beer's law............ 62
  in ethyl alcohol—Beer's law....... 61
  in methyl alcohol—Beer's law..... 61
  in water—Beer's law.............. 59
  in water—molecules constant...... 59
  with aluminium chloride........... 60
  with calcium chloride.............. 60

Gladstone, absorption spectra of chromium compounds.................. 63

Hartley, absorption spectra of chromium compounds............. 63
  criticizes the views of Donnan and Bassett................ 13
  on change in absorption with change in temperature......101
  on the absorption spectra of chromium compounds...... 64
  on the absorption spectra of copper salts................ 45
  on the absorption spectra of salts of neodymium......... 70
  on the absorption spectra of solutions of cobalt salts..... 12
  on the absorption spectrum of nickel salts................. 39
  on the absorption spectra of the nitrate of erbium....... 70
  work of...................... 5
Hydrate of cobalt salts................ 35
Hydrates in aqueous solutions......... 1

Introductory 1
Ions constant for cobalt chloride in water 15
for nickel chloride in water 40
Iron, salts of 59

Jones and Uhler—
absorption of cobalt chloride in methyl alcohol 17
cadmium zinc spark 8
on dehydration........ 37
on solvation........ 38
spectrograph........ 6
work on cobalt salts........ 11
Jones, on the absorption spectra of compounds of praseodymium and neodymium 69

Knoblauch, absorption spectra of chromium compounds........ 63
on the absorption spectra of copper salts 45
Krüss and Wilson, on the absorption spectra of the rare earths........ 68

Lapraik, on the absorption spectra of chromium compounds........ 64
Light, sources of........ 8
Liveing and Dewar, absorption spectra of chromium compounds 63
Liveing, on the effect of temperature on the absorption spectra of compounds of didymium and erbium........ 69

Melde, absorption spectra of chromium compounds........ 63
Methods of work........ 3
Methyl alcohol—
and water—copper bromide in.... 54
and water—neodymium chloride in mixtures of........ 79
and water—neodymium nitrate in mixtures of........ 93
cobalt bromide in—Beer's law..... 25
cobalt chloride in—Beer's law..... 16
copper bromide in—Beer's law..... 52
copper chloride in—Beer's law..... 46
copper chloride in—with water 49
ferric chloride in—Beer's law...... 61
neodymium chloride in—Beer's law 77
neodymium nitrate in—Beer's law. 91
with water, cobalt bromide in 27
with water, cobalt chloride in...... 19
Miner, H. S........Preface, 71
Moissan, absorption spectra of chromium compounds 63
Molecules constant for—
chromium chloride in water....... 65
chromium nitrate in water 67
cobalt bromide in water........ 22
cobalt chloride in water........ 15
cobalt nitrate in water........ 30
cobalt sulphocyanate in water..... 33
copper bromide in water........ 52
copper chloride in water........ 46
copper nitrate in water........ 56
ferric chloride in water........ 59
Molecules constant for—
neodymium chloride in water...... 76
neodymium nitrate in water....... 91
nickel chloride in water........ 41
Müller, absorption spectra of chromium compounds........ 63
dissociation can not account for deviations from Beer's law ...103
on the absorption spectra of copper salts........ 45
on the absorption spectra of nickel and copper salts.......100
on the absorption spectrum of nickel salts........ 39
work of........ 5
Muthmann and Stützel, on the absorption spectra of salts of neodymium... 70
Muthmann, on the absorption spectra of compounds of praseodymium and neodymium........ 69

Neodymium bromide in water—Beer's law........ 86
Neodymium chloride, anhydrous....... 84
Neodymium chloride in—
ethyl alcohol and water........ 83
ethyl alcohol—Beer's law........ 78
methyl alcohol—Beer's law........ 77
mixtures of methyl alcohol and water........ 79
water—Beer's law........ 72
water—molecules constant........ 76
water with calcium and aluminium chlorides........ 77
Neodymium nitrate in—
acetone—Beer's law........ 92
ethyl alcohol—Beer's law........ 92
methyl alcohol—Beer's law........ 91
mixtures of acetone and water..... 94
mixtures of methyl alcohol and water........ 93
water—Beer's law........ 87
water—molecules constant........ 91
Neodymium, salts of........ 68
Nernst filament........ 10
lamp........ 9
Nickel acetate in water—Beer's law.... 43
Nickel chloride in water—
Beer's law........ 39
ions constant........ 40
molecules constant........ 41
with calcium and aluminium chlorides........ 41
Nickel, salts of........ 39
sulphate in water—Beer's law.. 42

Ostwald........ 1
on absorption spectra........ 63
on the color of solutions of cobalt salts........ 12
Ostwald's theory of absorption spectra..100

Photographic material........ 7
Potilitzin, on the color changes in cobalt salts........ 11

Praseodymium chloride in—
    mixtures of the alcohols and water. 95
    water—Beer's law................ 94
Praseodymium nitrate in water—Beer's law................................ 96
Praseodymium, salts of................ 68
Pulfrich, absorption spectra of chromium compounds........................ 63

Rech, on the absorption spectra of aqueous solutions of neodymium chloride. 71
Recoura, absorption spectra of chromium compounds...................... 63
Results obtained in this work..........103
Röntgen coil........................... 9
Russell, on the absorption spectra of solutions of cobalt salts.............. 11

Sabatier, absorption spectra of chromium compounds...................... 63
Schaeffer, Helen....................... 98
    on the absorption spectra of the rare earths. 70
Scheele, on the absorption spectra of praseodymium compounds........... 68
Schottländer, on the absorption spectra of the rare earths.................. 68
Schunck, absorption spectra of chromium compounds...................... 63
Settegast, absorption spectra of chromium compounds.................... 63
Solutions, absorption spectra of........ 1
Solvation.............................. 2
    and absorption..................101
    Uhler and Jones.................. 38
Soret, absorption spectra of chromium compounds..................... 63
    on the absorption spectrum of nickel chloride....................... 39
Sources of light....................... 8
Spectra, absorption, of solutions....... 1
Spectrogram, making a................ 9
Stützel and Muthmann, on the absorption spectra of salts of neodymium... 70

Summary and conclusions.............100
    of results with cobalt salts... 35

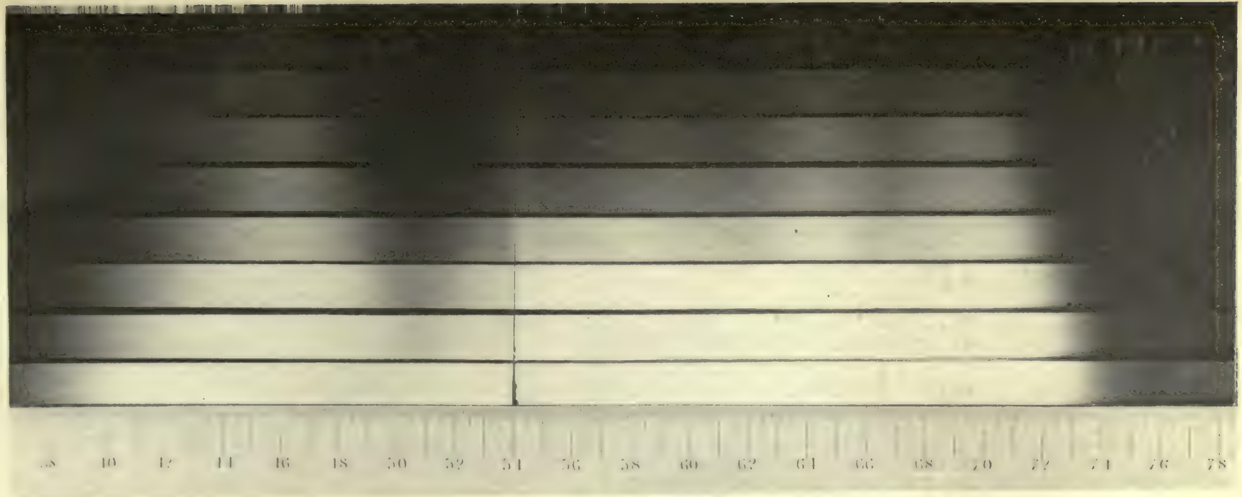
Talbot, absorption spectra of chromium salts................................ 63
Temperature, effect of on absorption...101
Theories of absorption.................101
Tichborne, on the color changes in cobalt salts.......................... 11

Uhler and Jones—
    absorption of cobalt chloride in methyl alcohol................ 17
    cadmium zinc spark............... 8
    Carnegie Publication No. 60...... Preface, 1
    on dehydration................... 37
    on solvation..................... 38
    spectrograph..................... 6
    work on cobalt salts.............. 11
Urbain, on the separation of the rare earths............................. 70

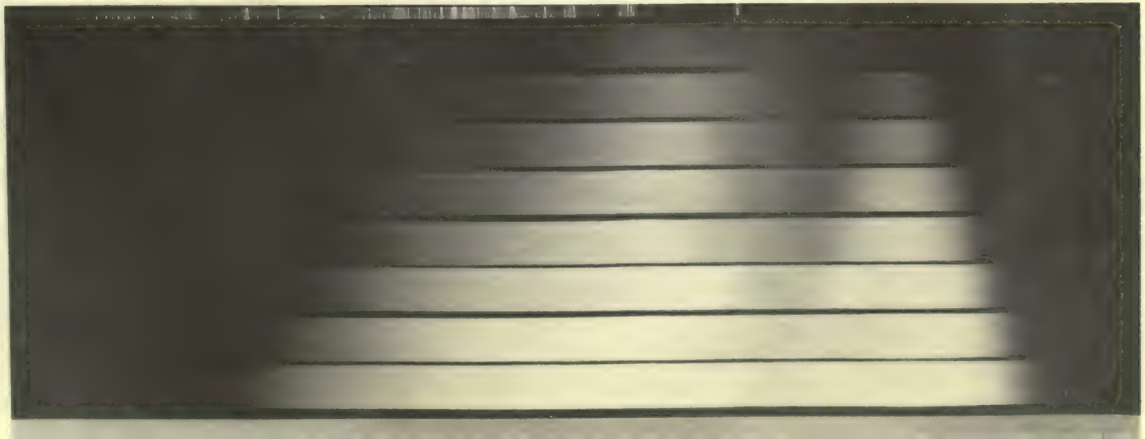
Vernon, on the absorption spectra of chromium compounds............... 64
Vierordt, absorption spectra of chromium compounds..................... 63
Vogel, absorption spectra of chromium compounds................... 63
    on the absorption spectrum of nickel chloride...................... 39

Wainwright and Wratten............. 7
Welsbach Light Co.............Preface, 71
Wiedermann, E., absorption spectra of chromium compounds............... 63
Wilson and Krüss, on the absorption spectra of the rare earths........... 68
Wratten and Wainwright.............. 7
Wyrouboff, on the color changes in cobalt salts......................... 12

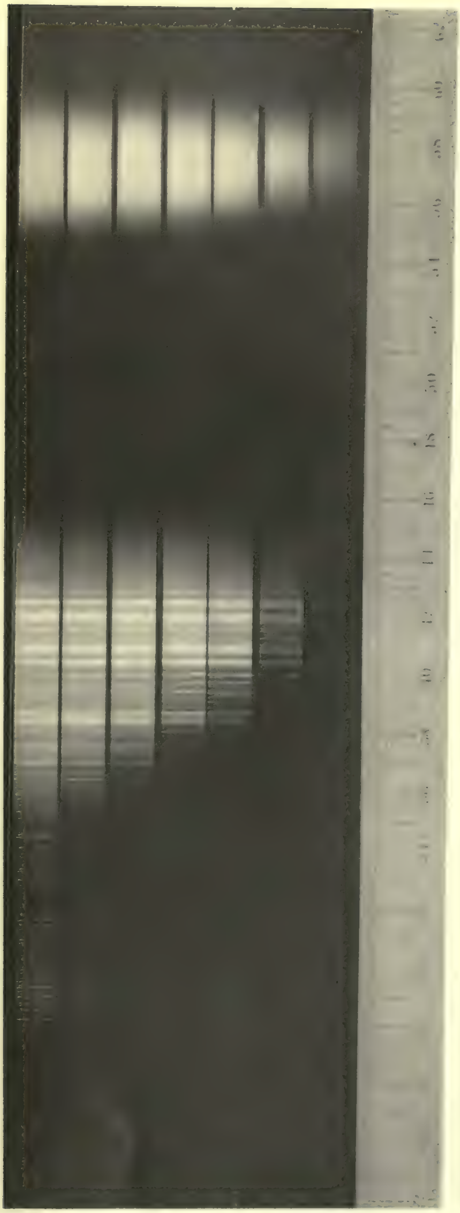
Zimmermann, absorption spectra of chromium compounds............... 63


38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70 72 74 76 78

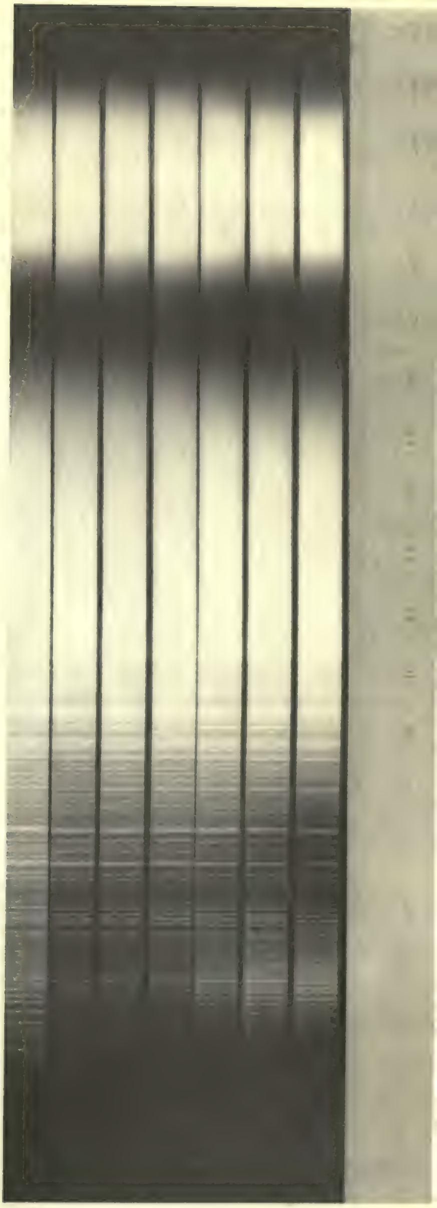
A



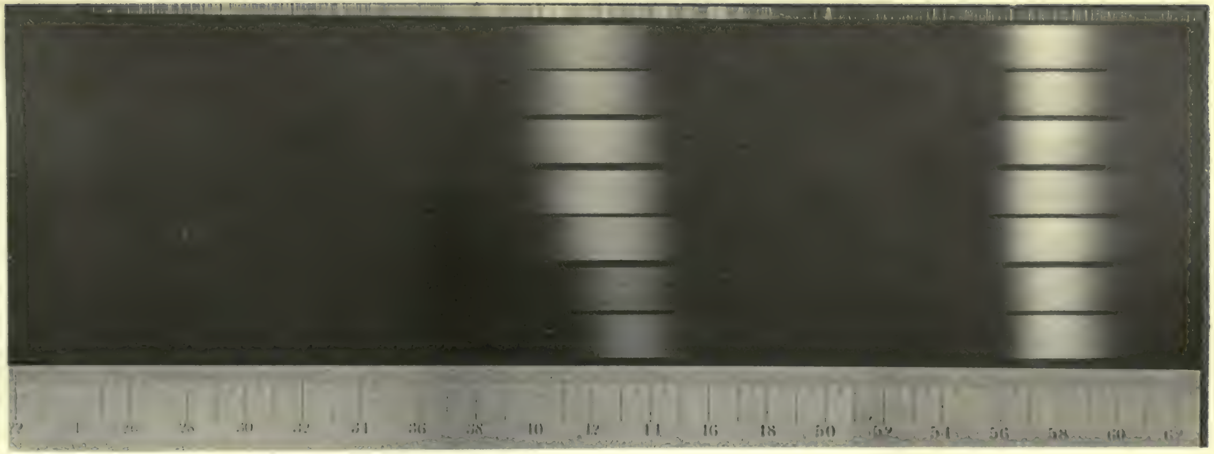
B



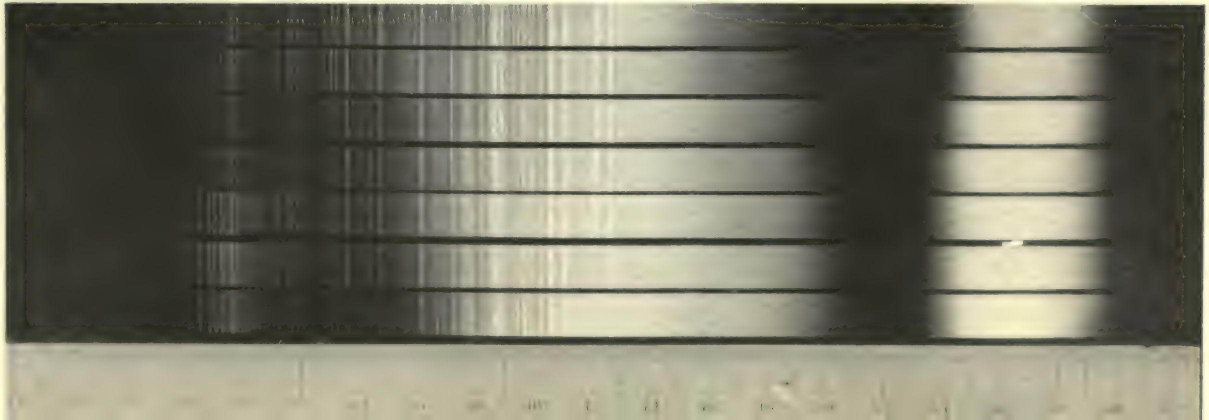
A



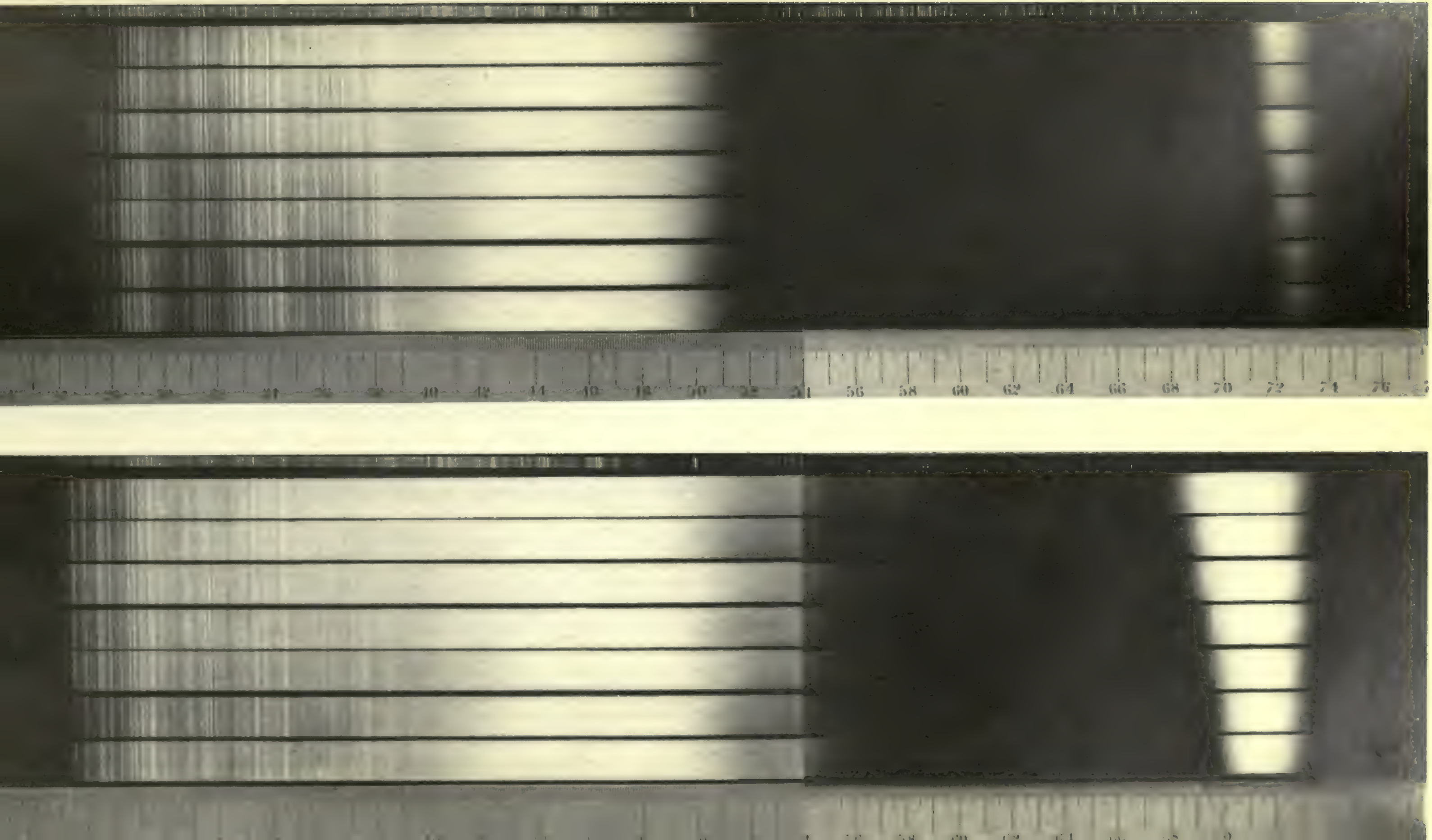
B

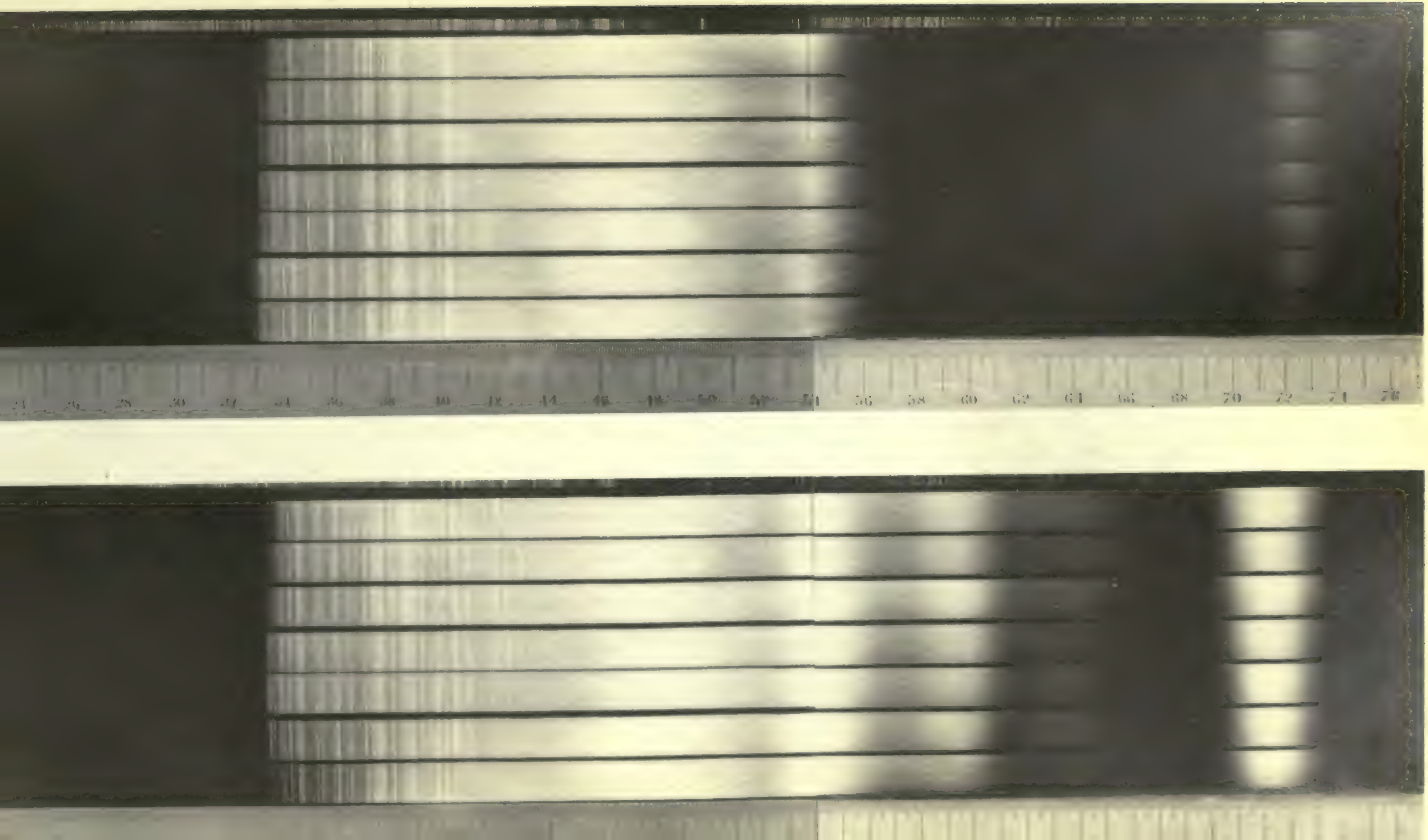

22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62

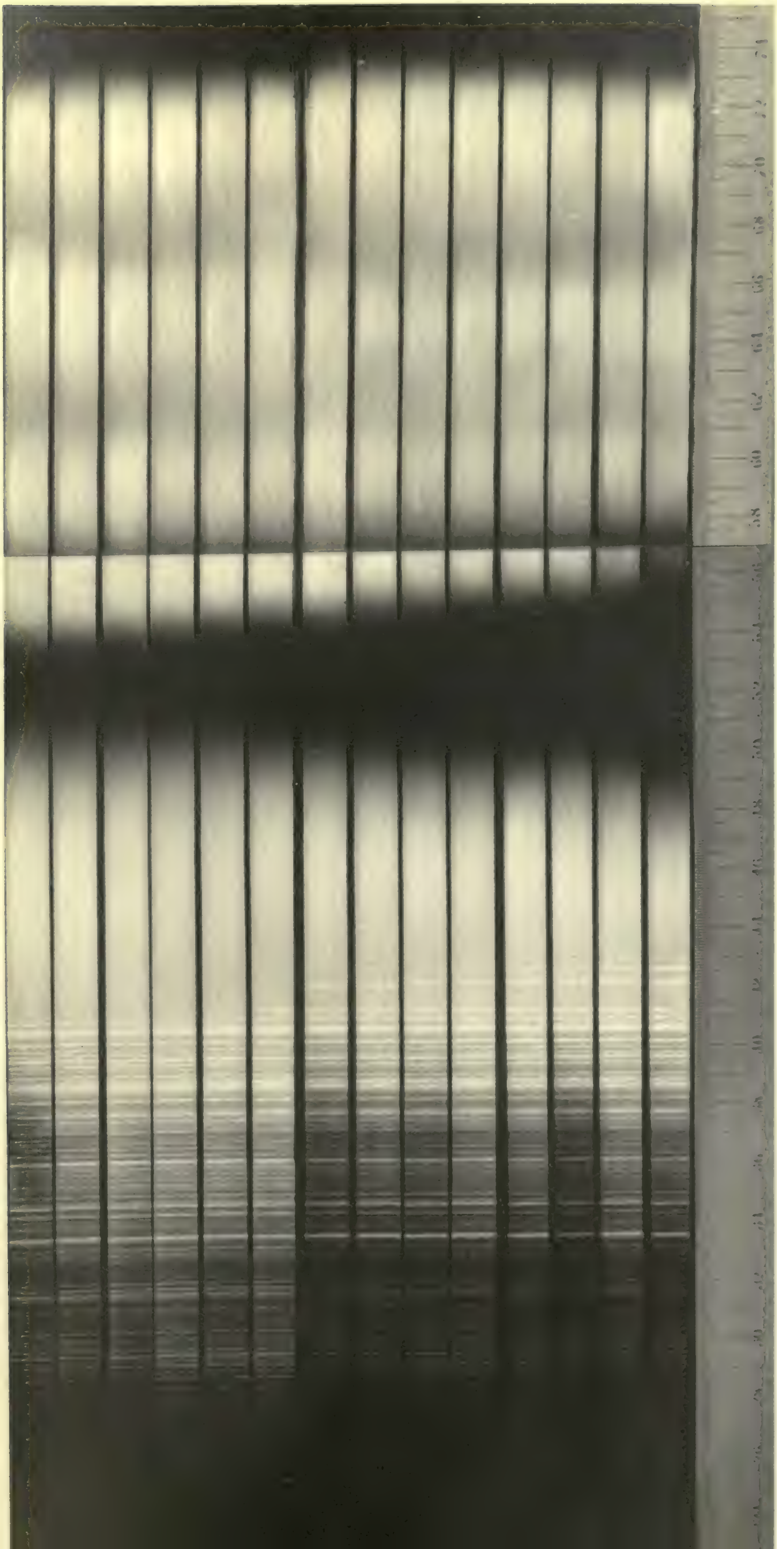
A

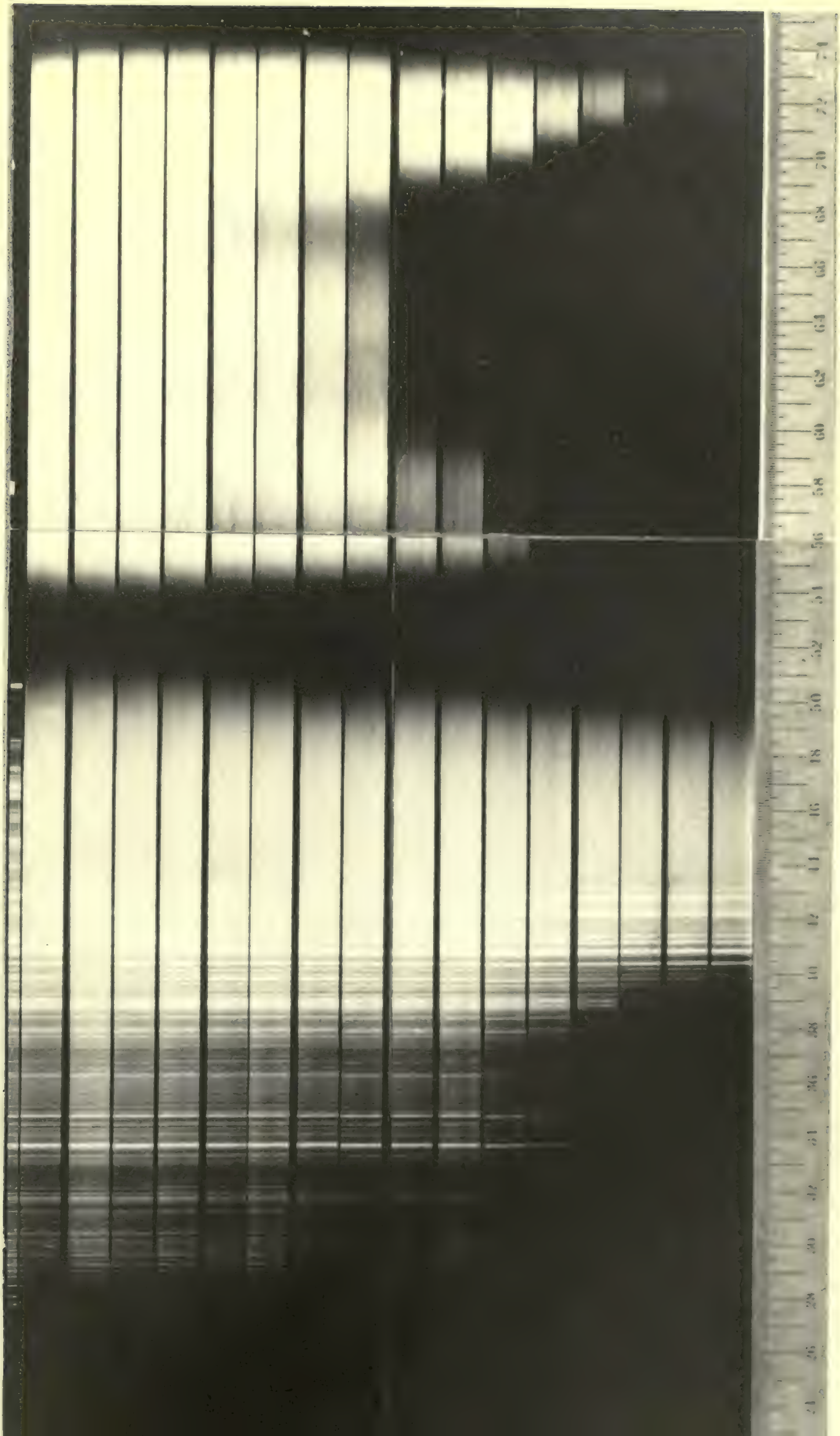


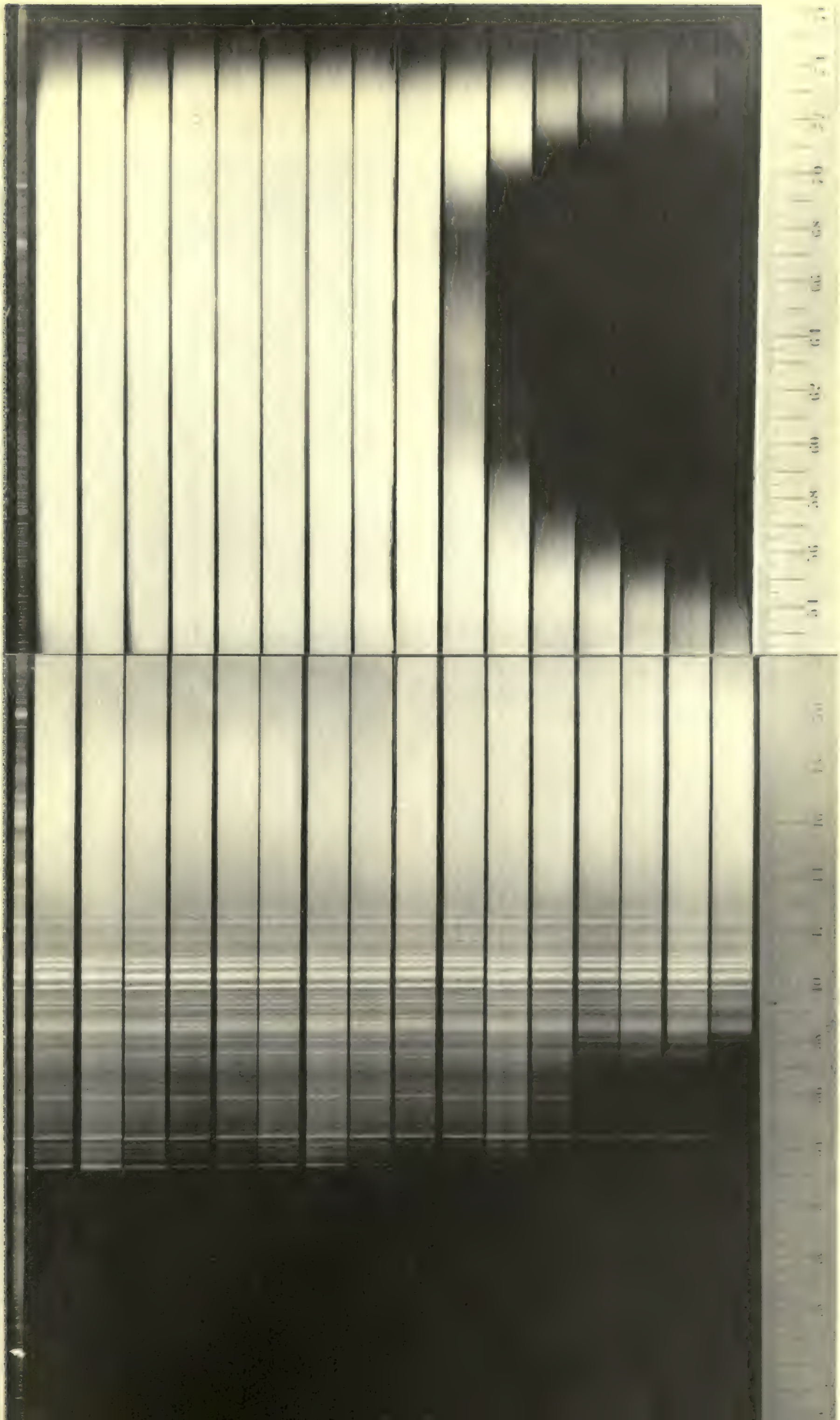
B

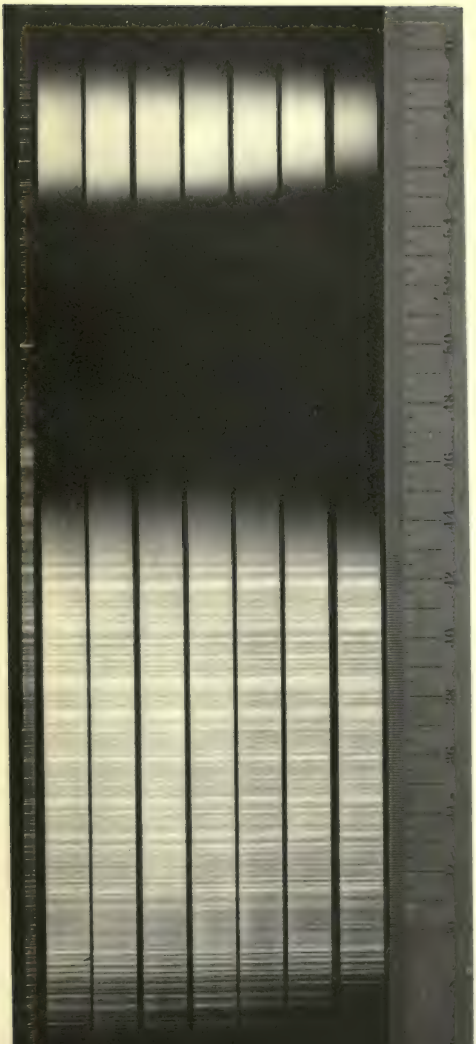

40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72
74
76


24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72
74
76

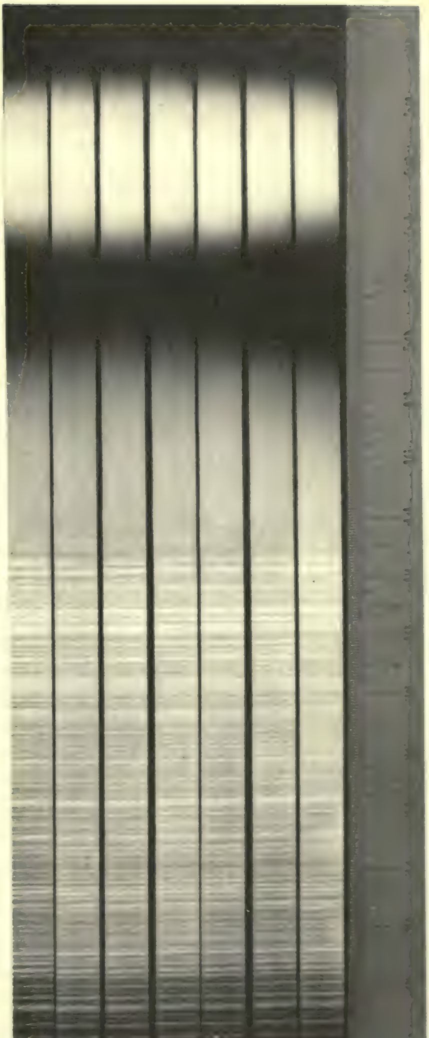



24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72
74

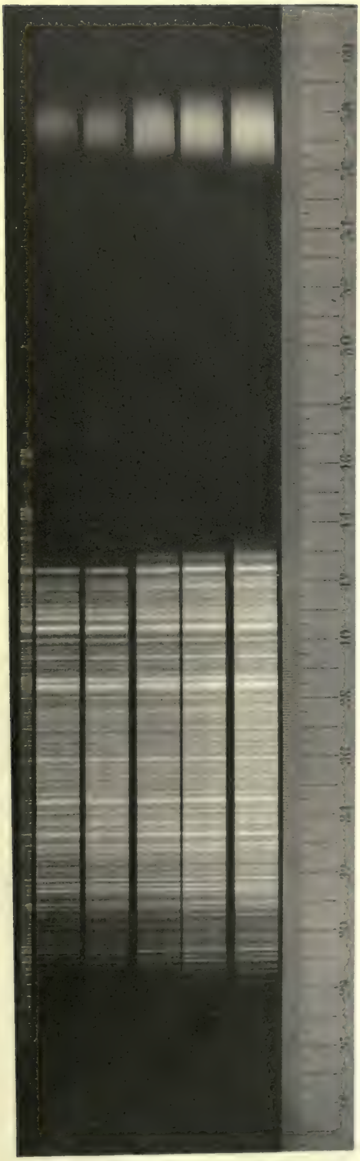




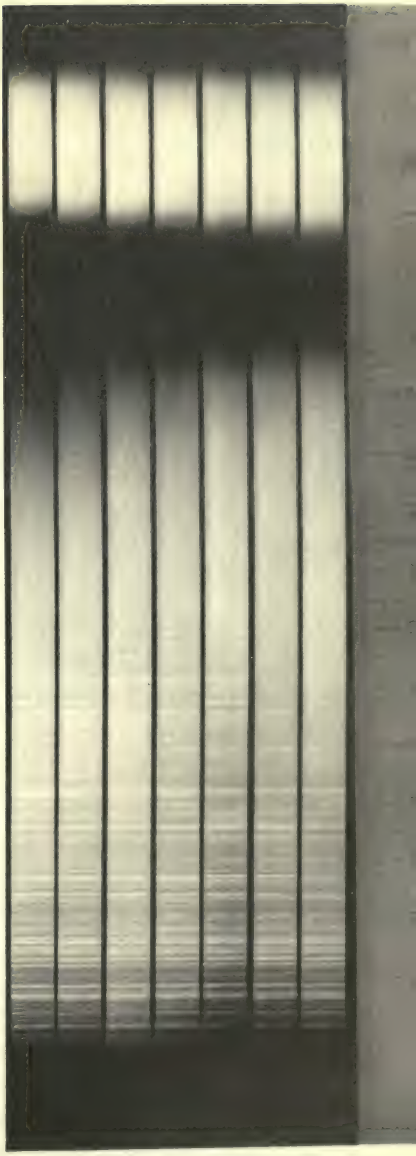
A



B

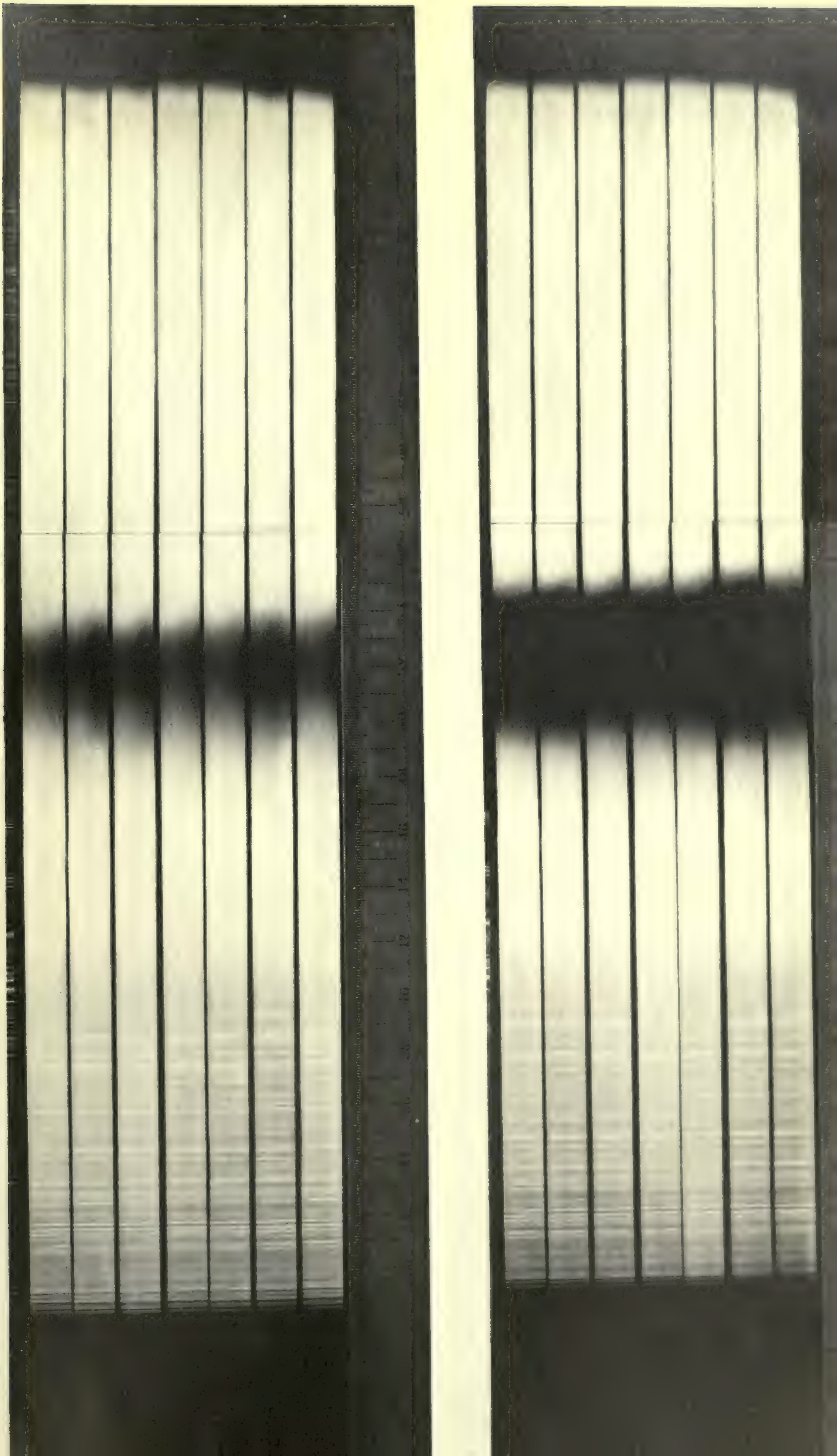


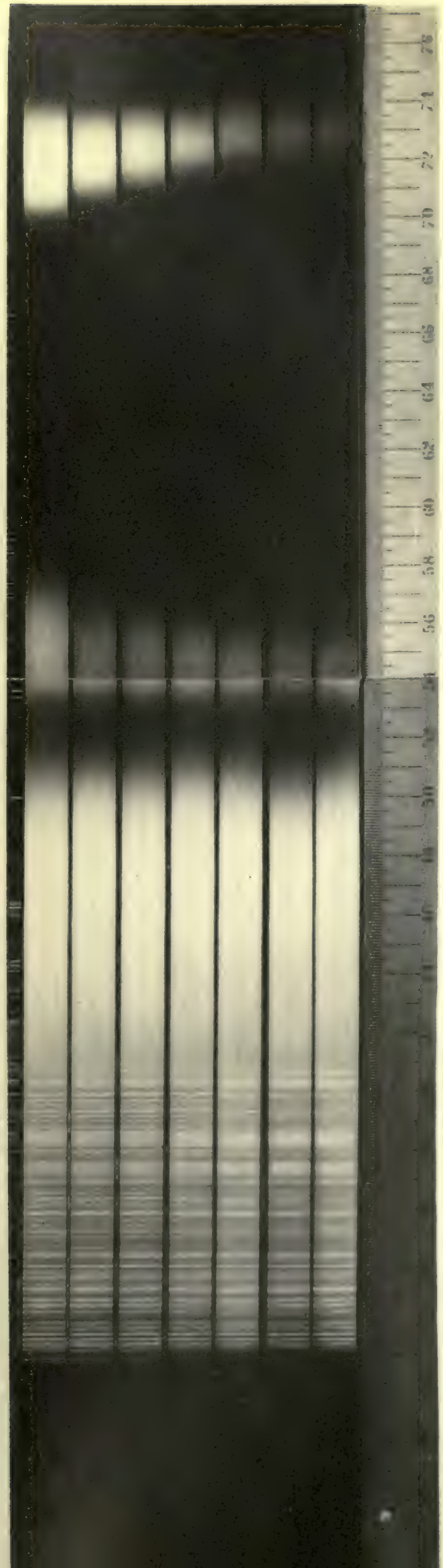
A

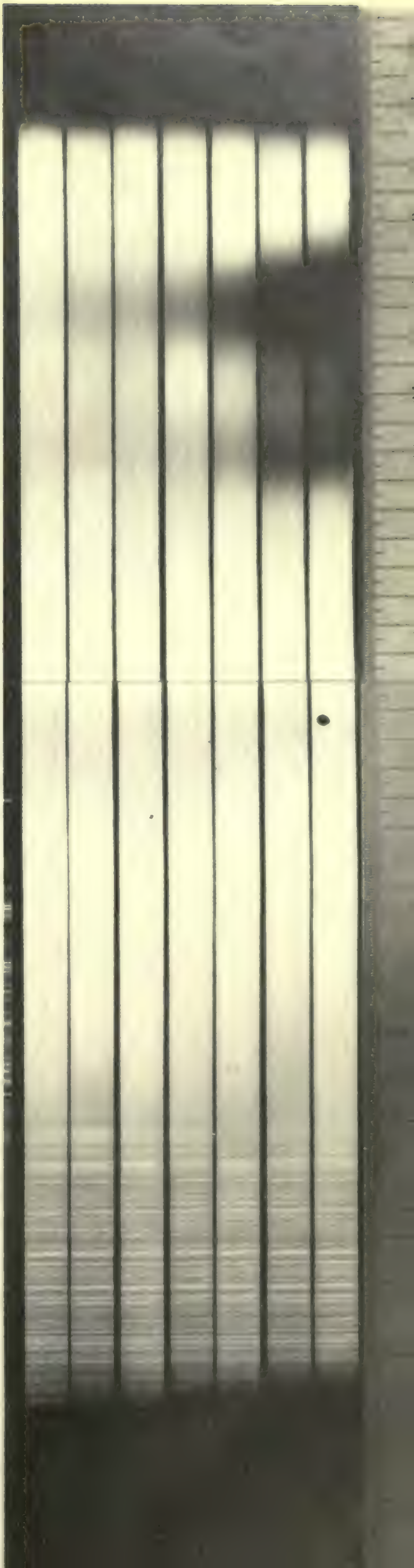


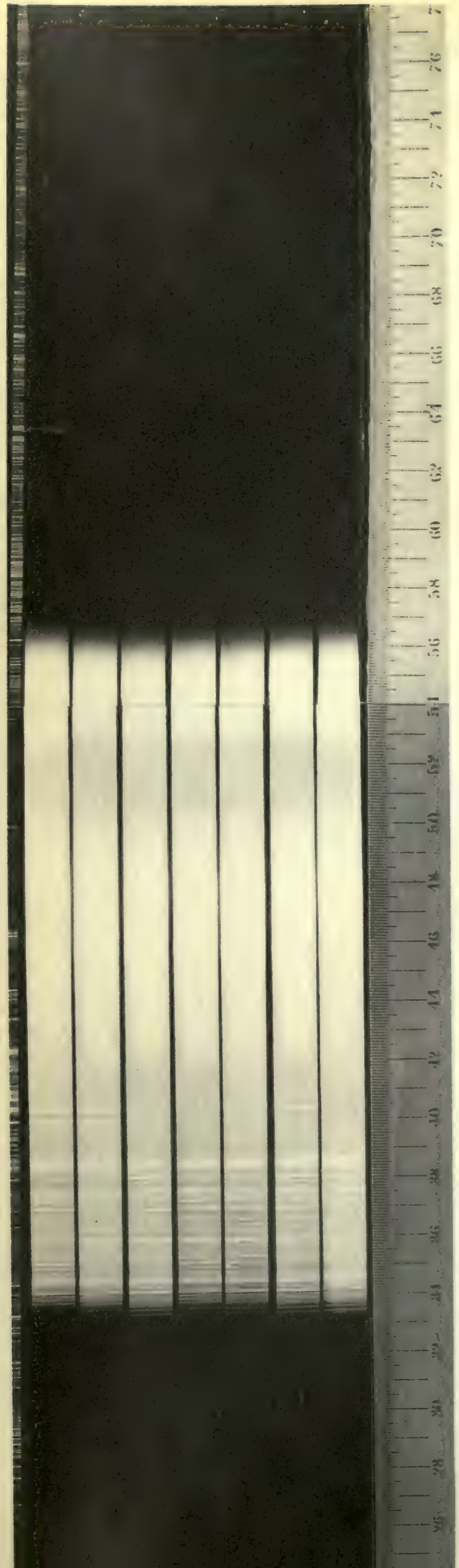
B

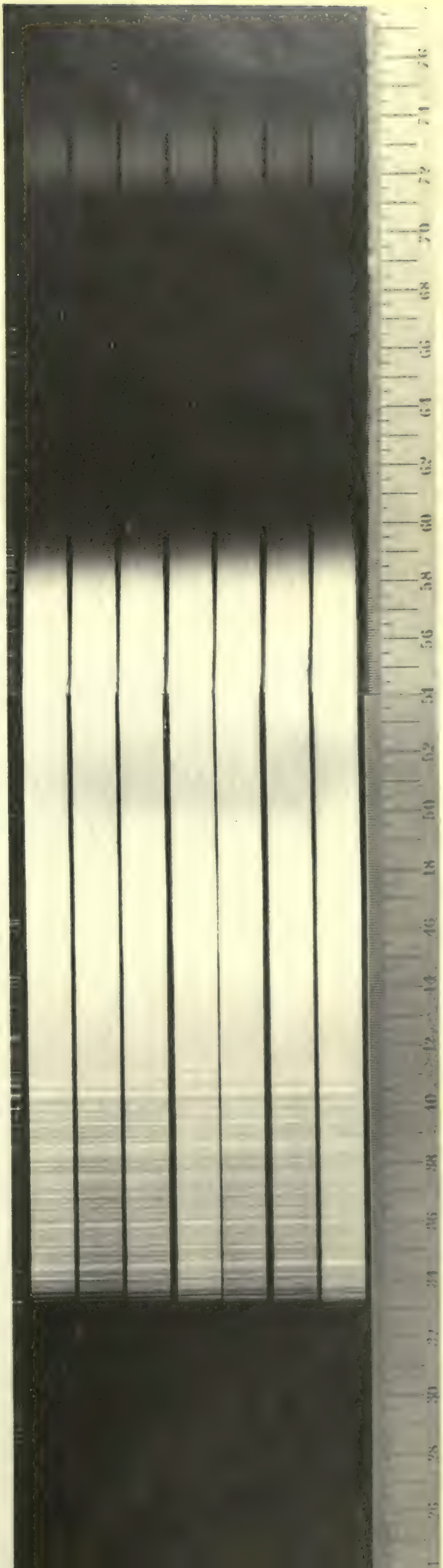
60
62
64
66
68
70

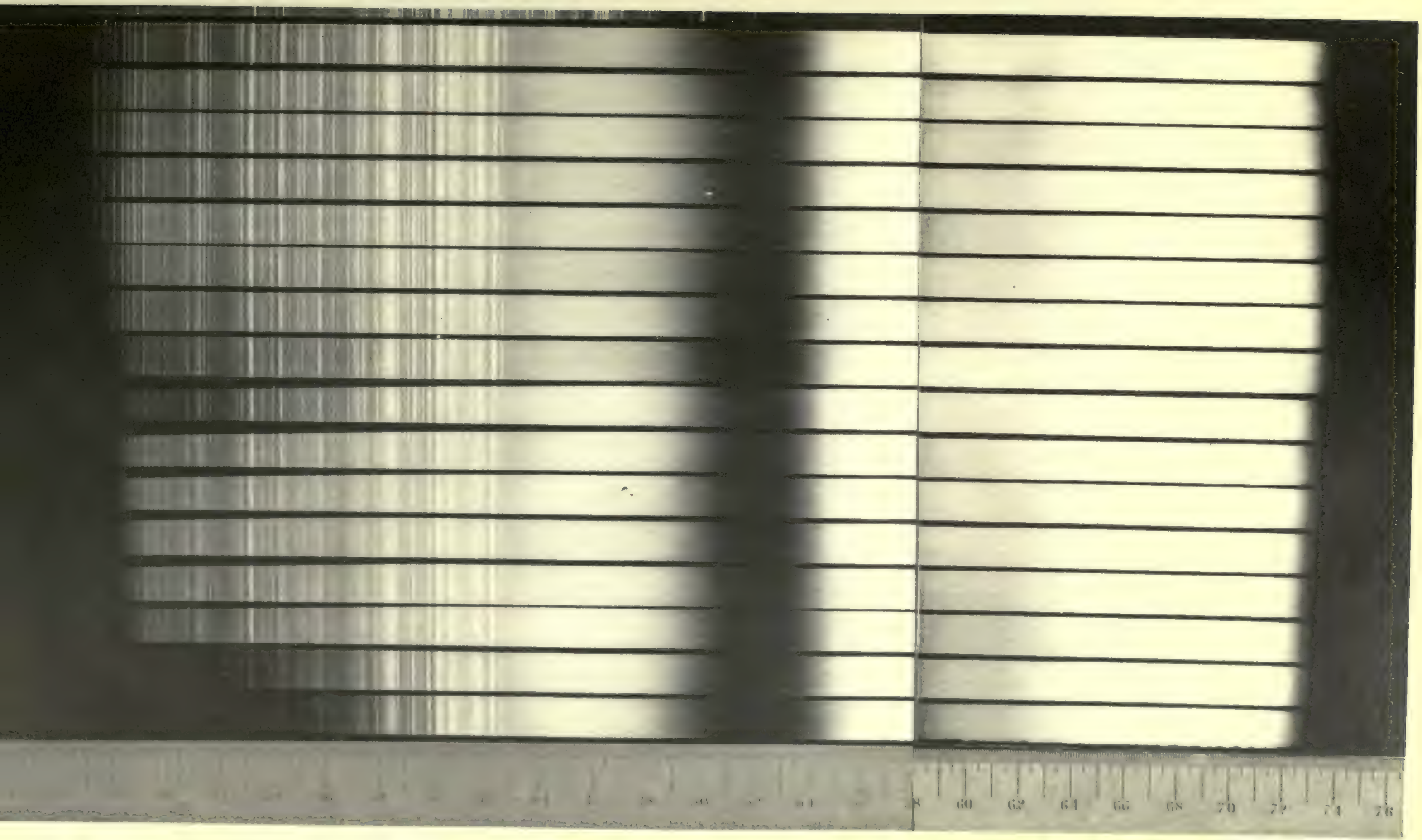


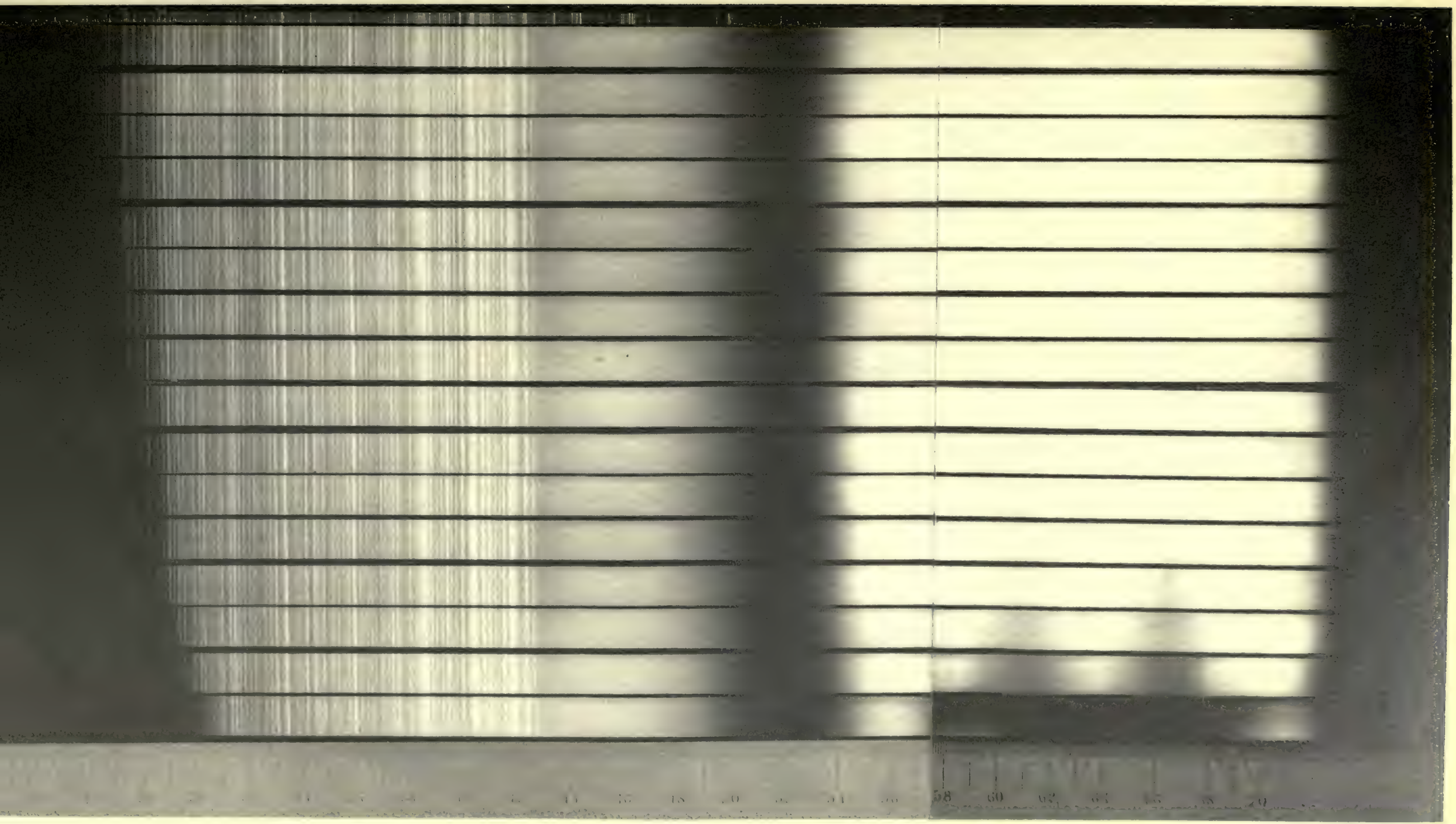

76
74
72
70
68
66
64
62
60
58
56

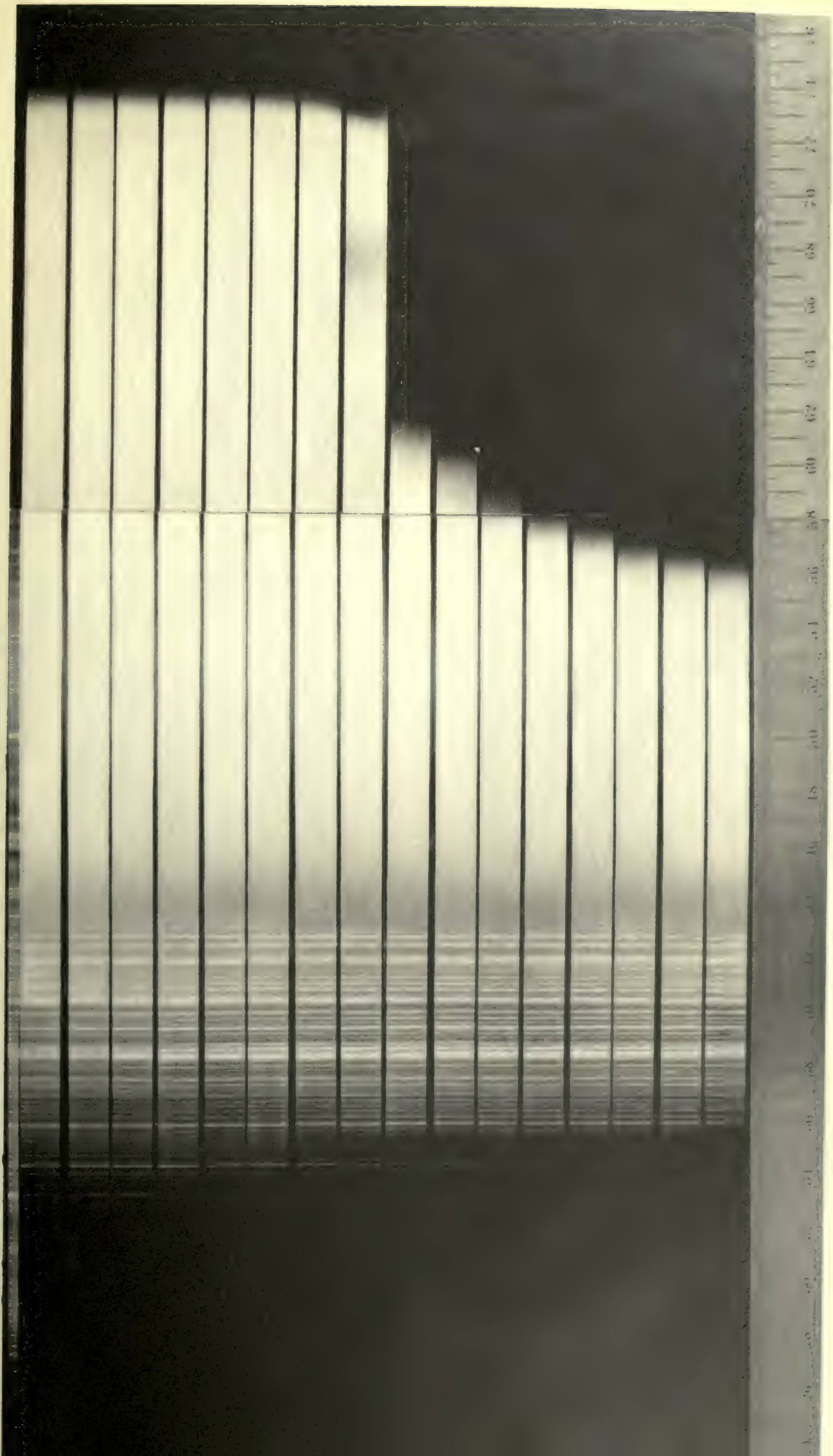


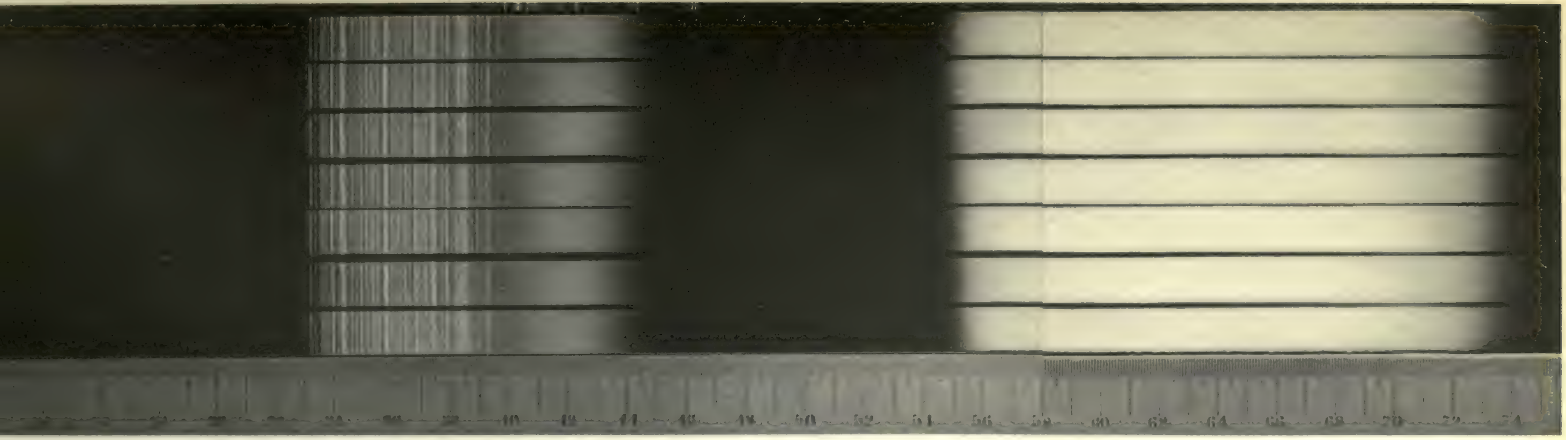

76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

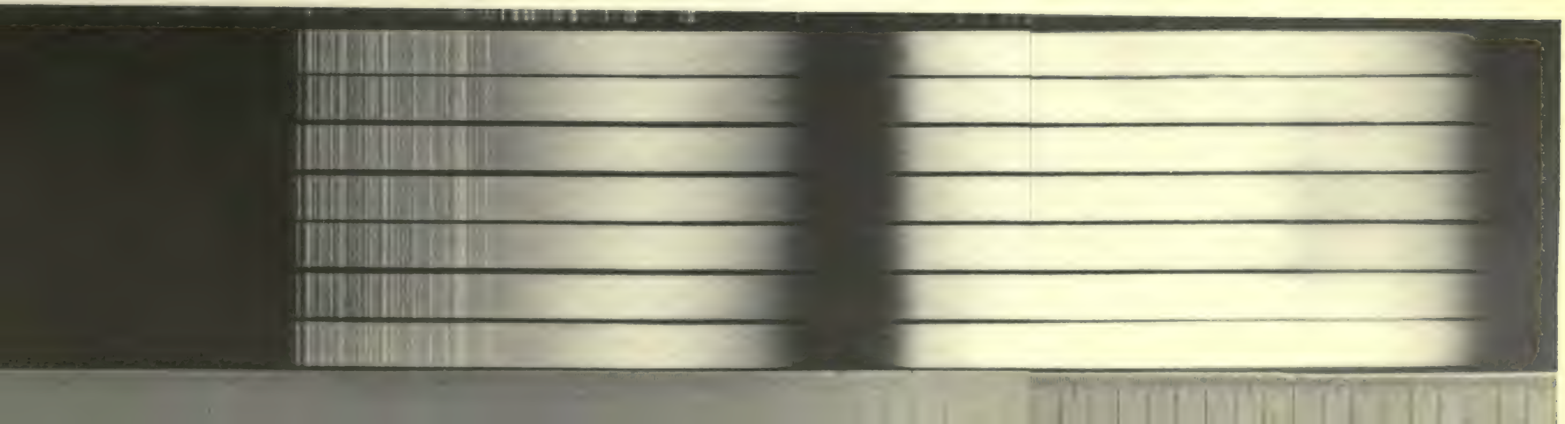

76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

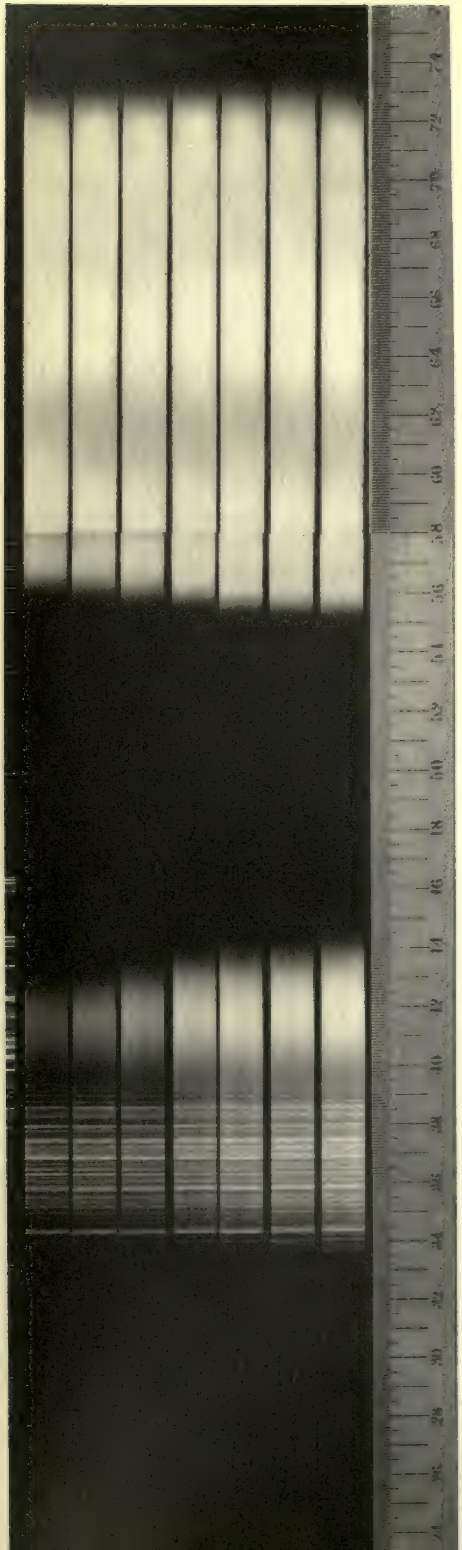

60
62
64
66
68
70
72
74
76

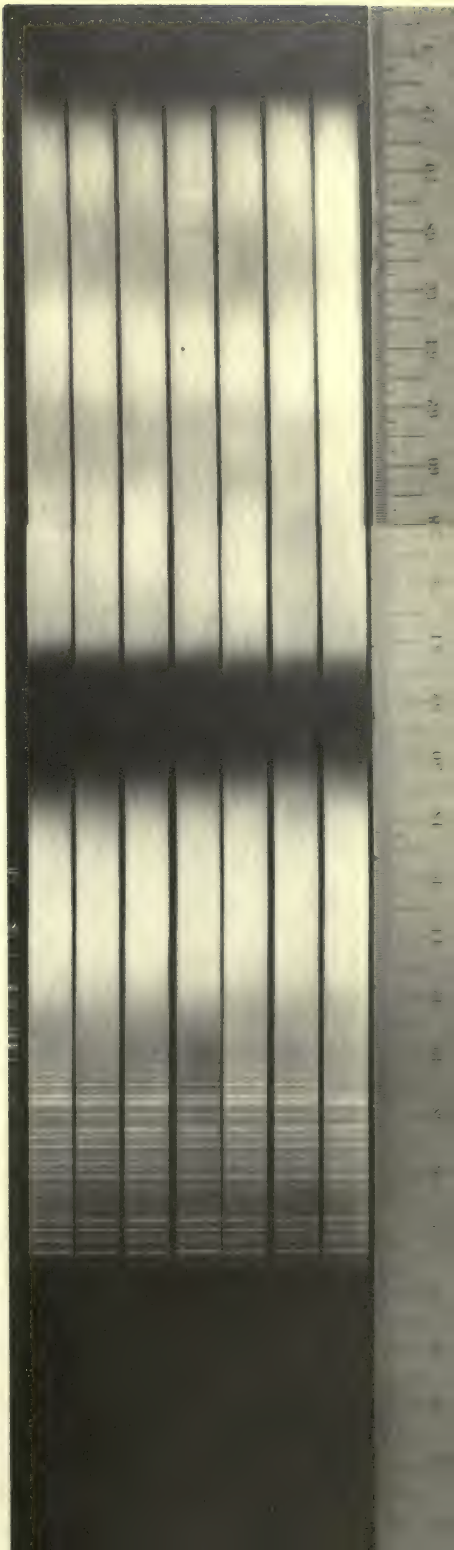

58
60

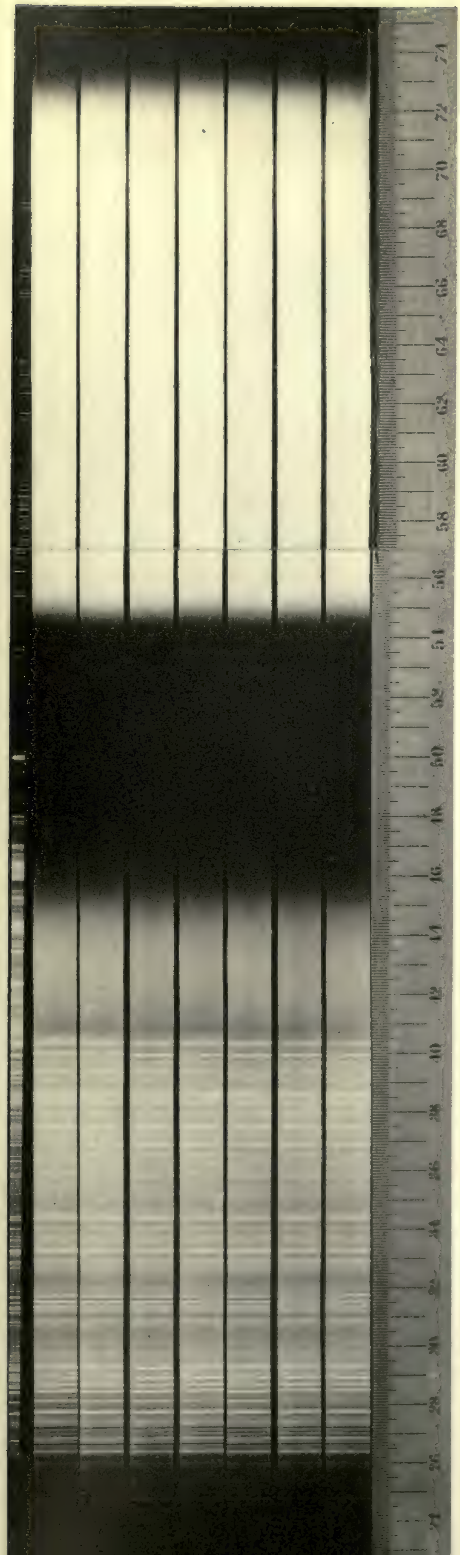


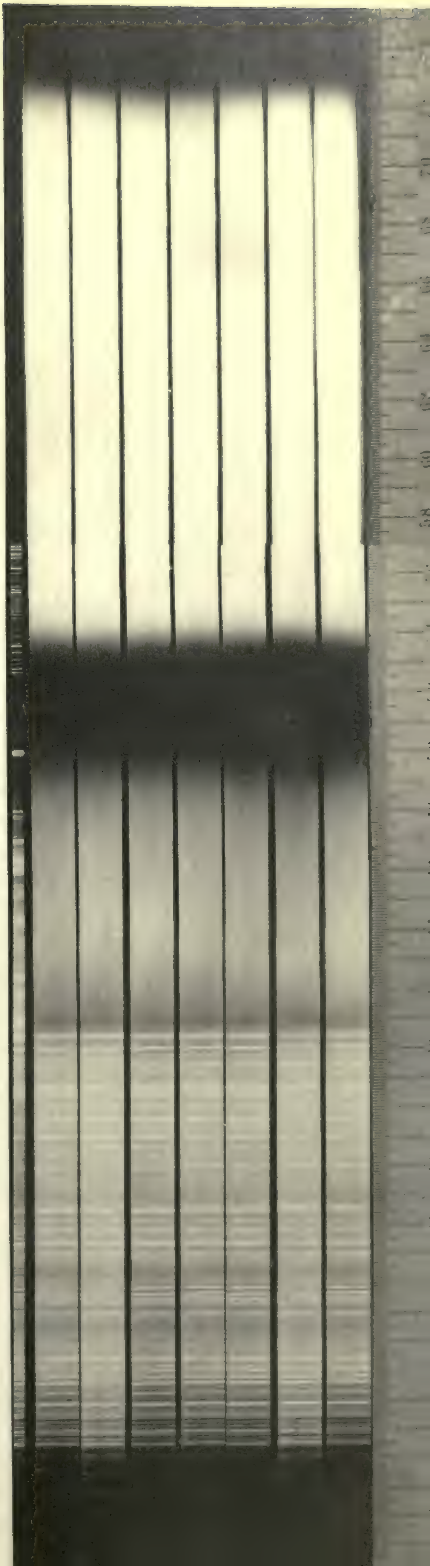

40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72
74

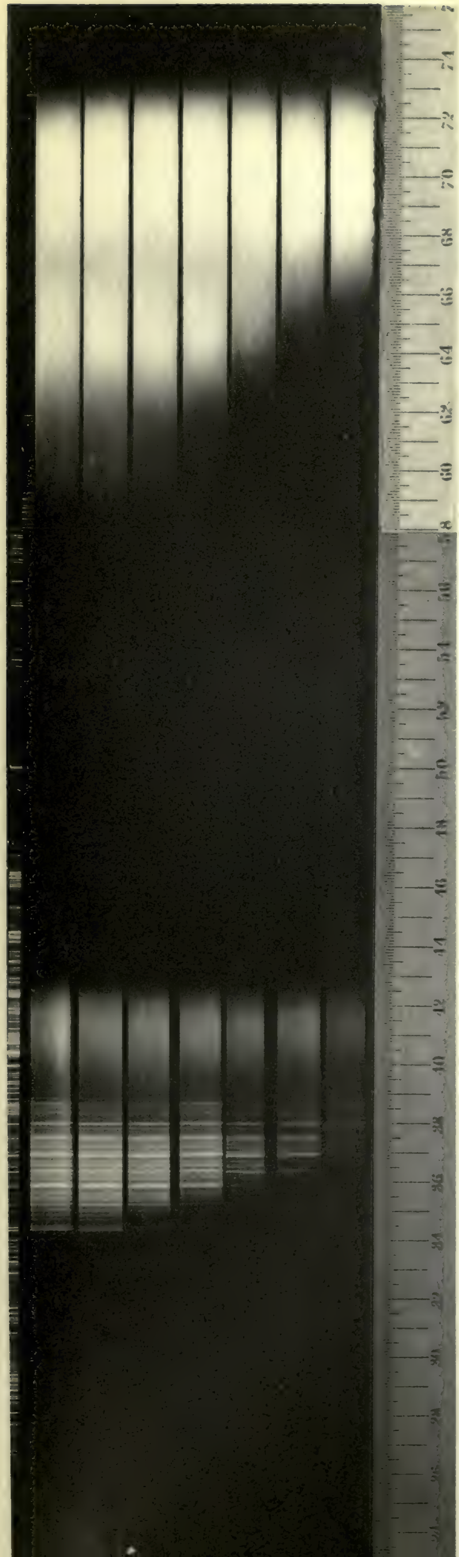


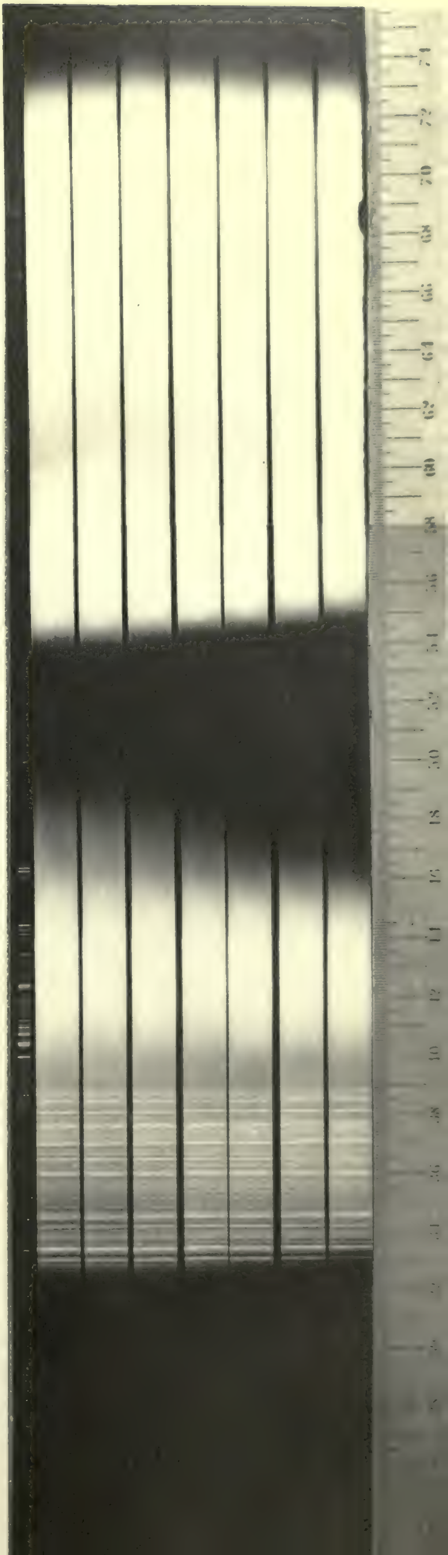

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

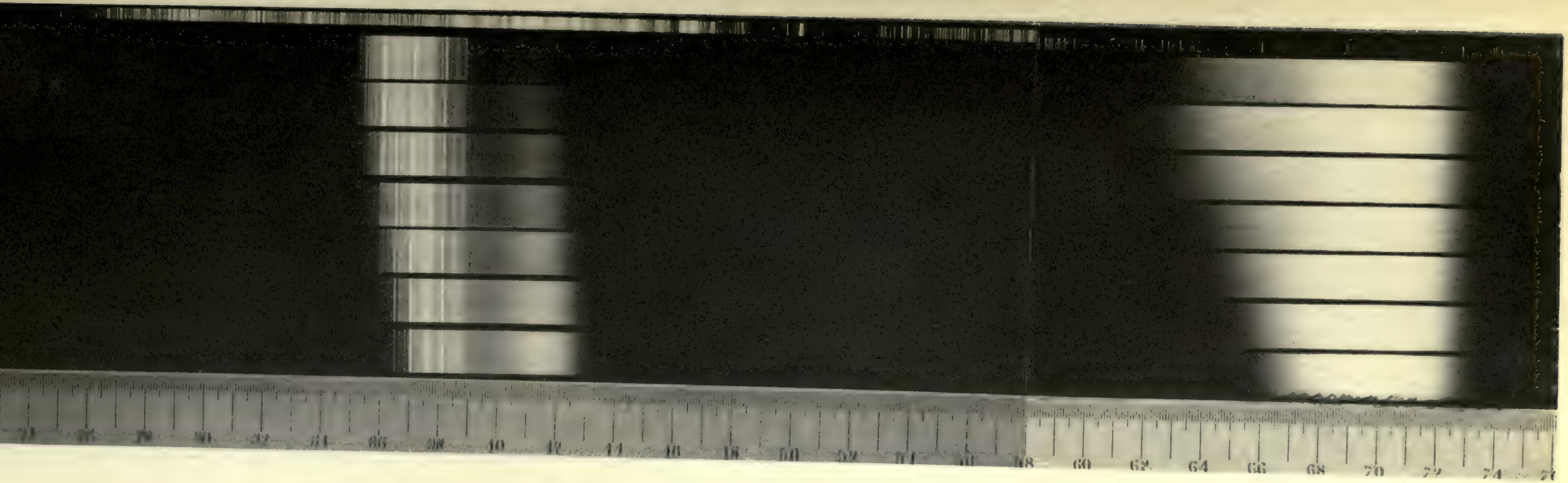


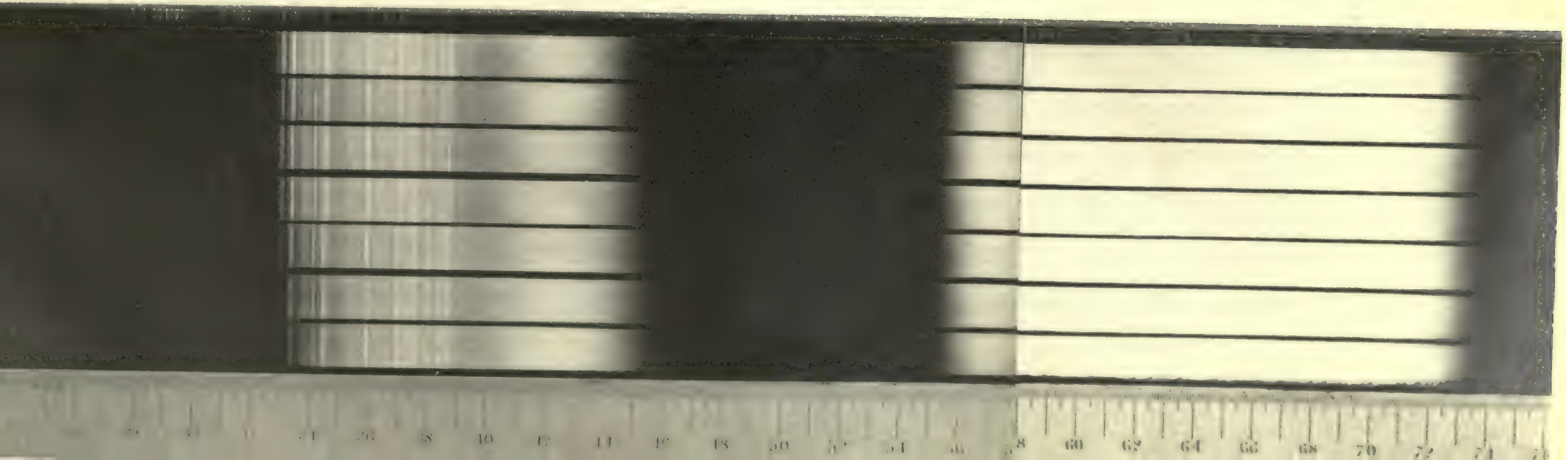

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24


70
68
66
64
62
60
58

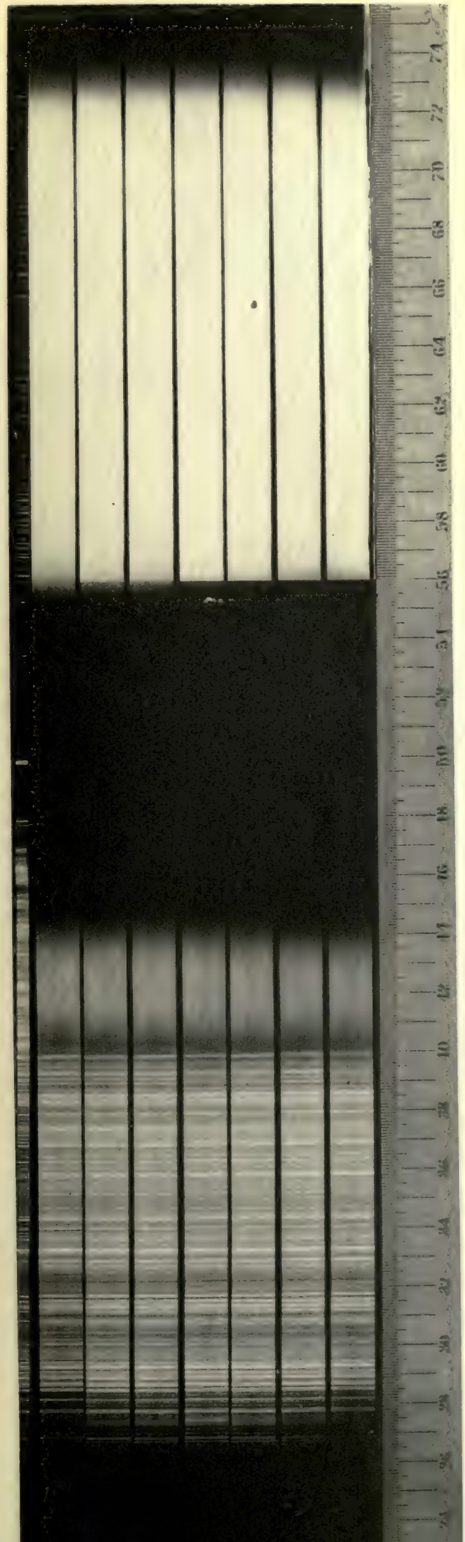

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

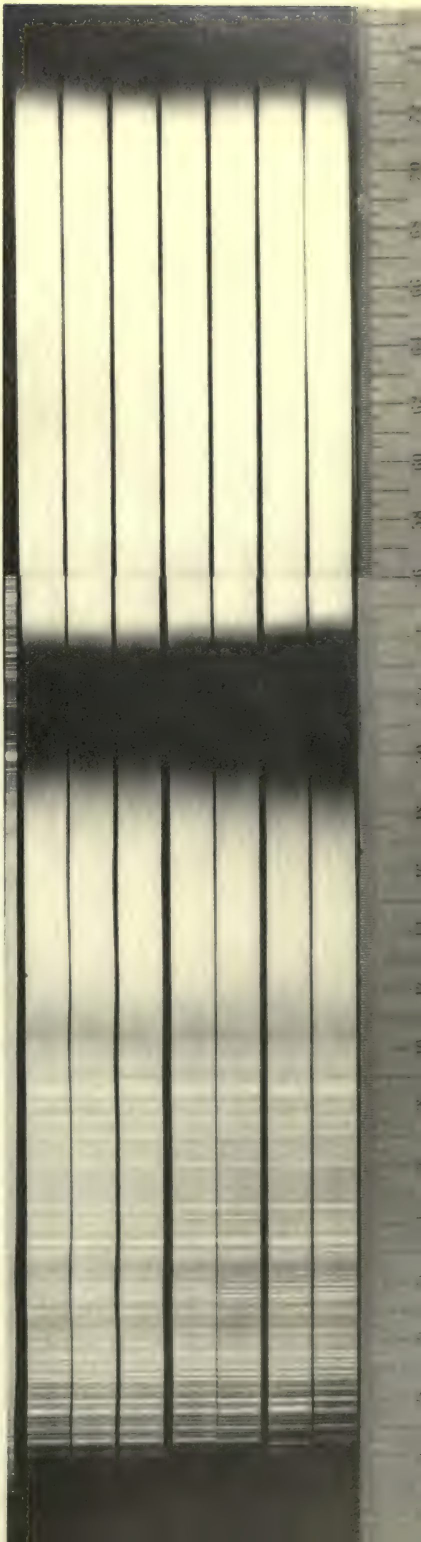

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34


24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72
74
76

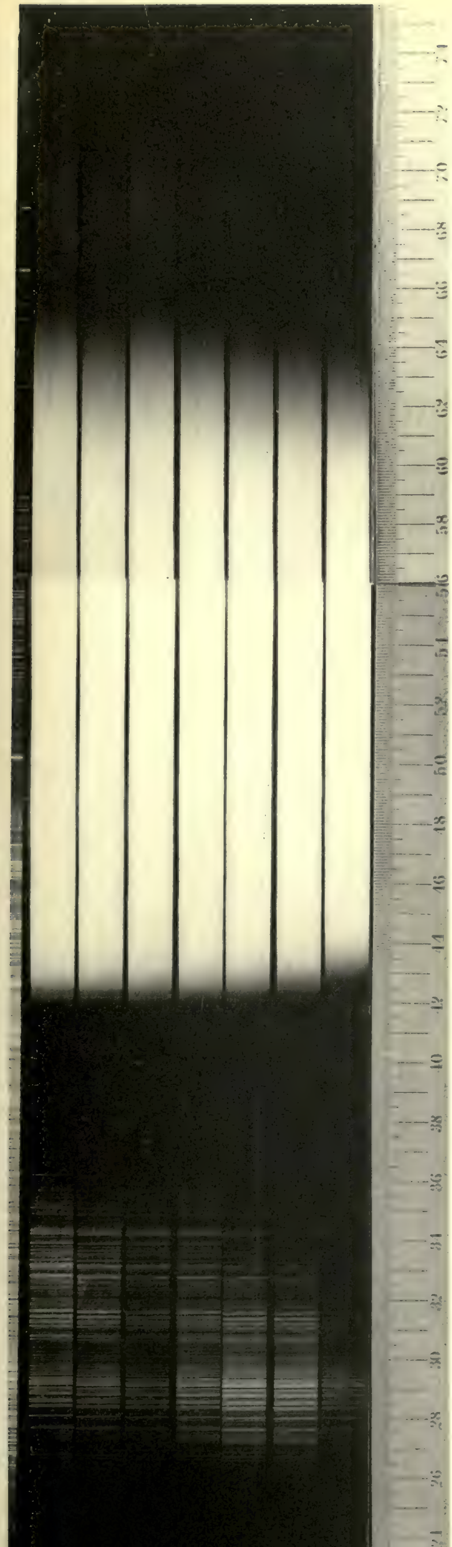

24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72
74
76

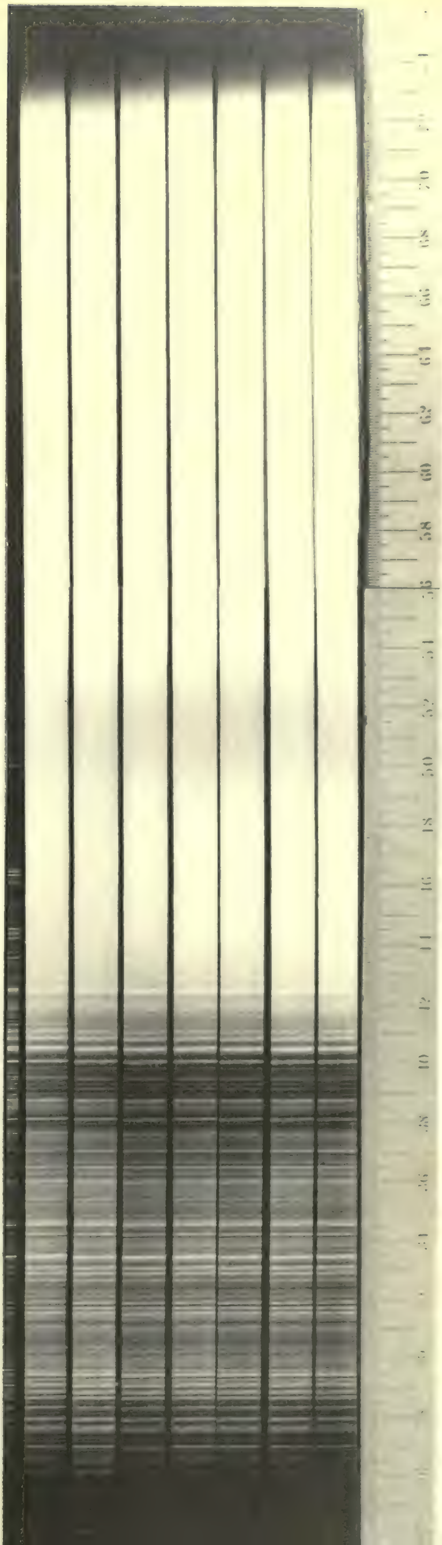
Fig

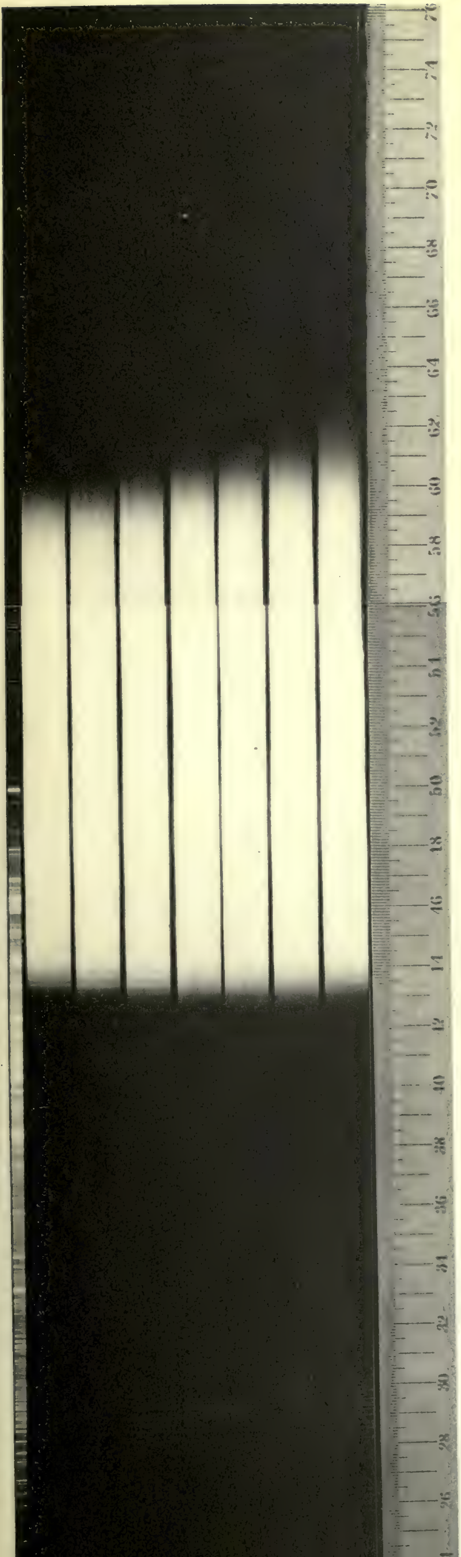

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24


72
70
68
66
64
62
60
58

PLATE


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34


76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

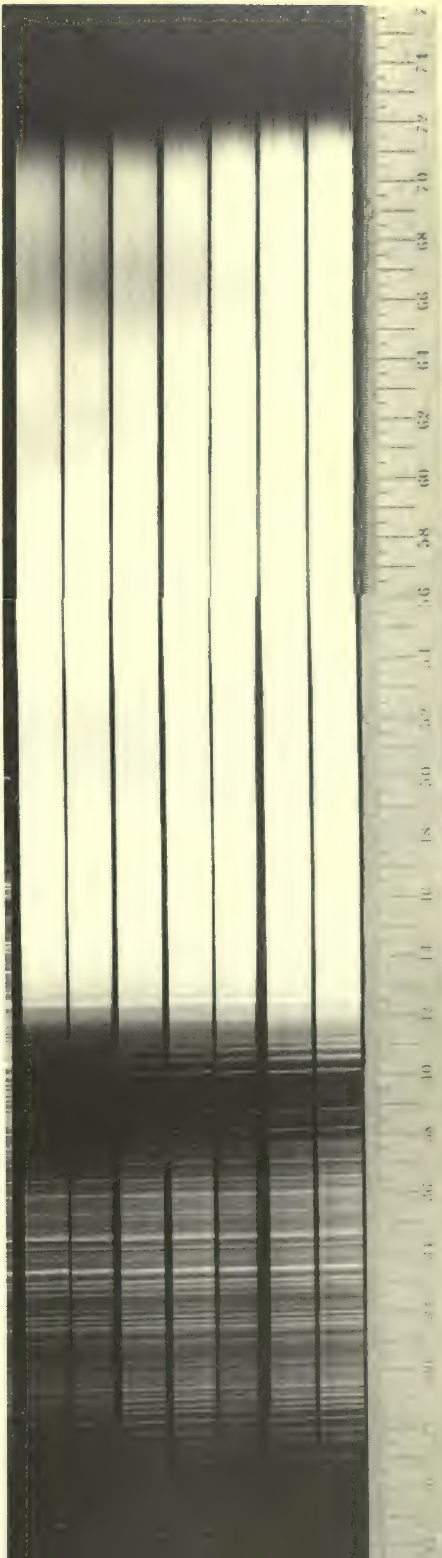
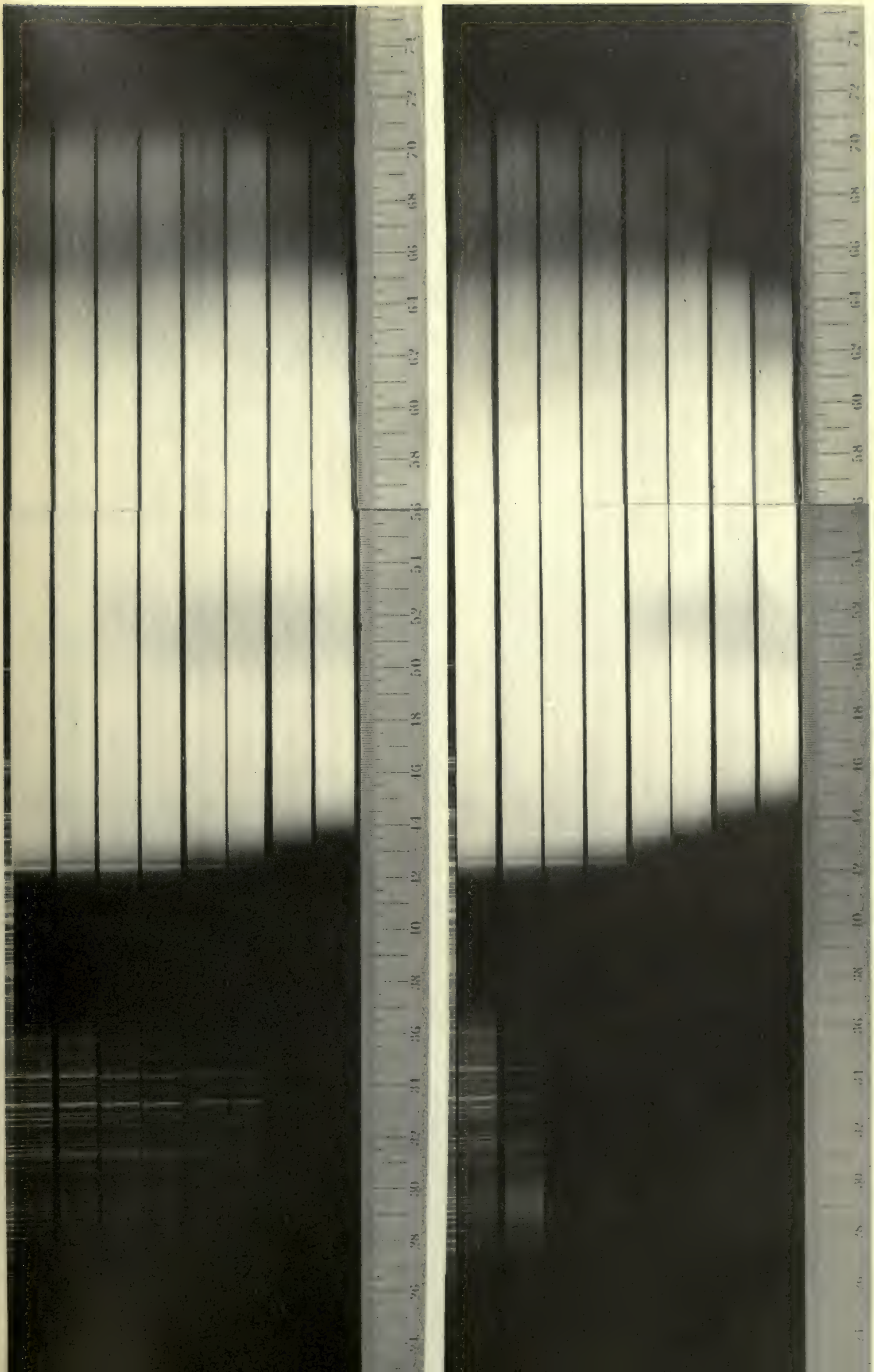
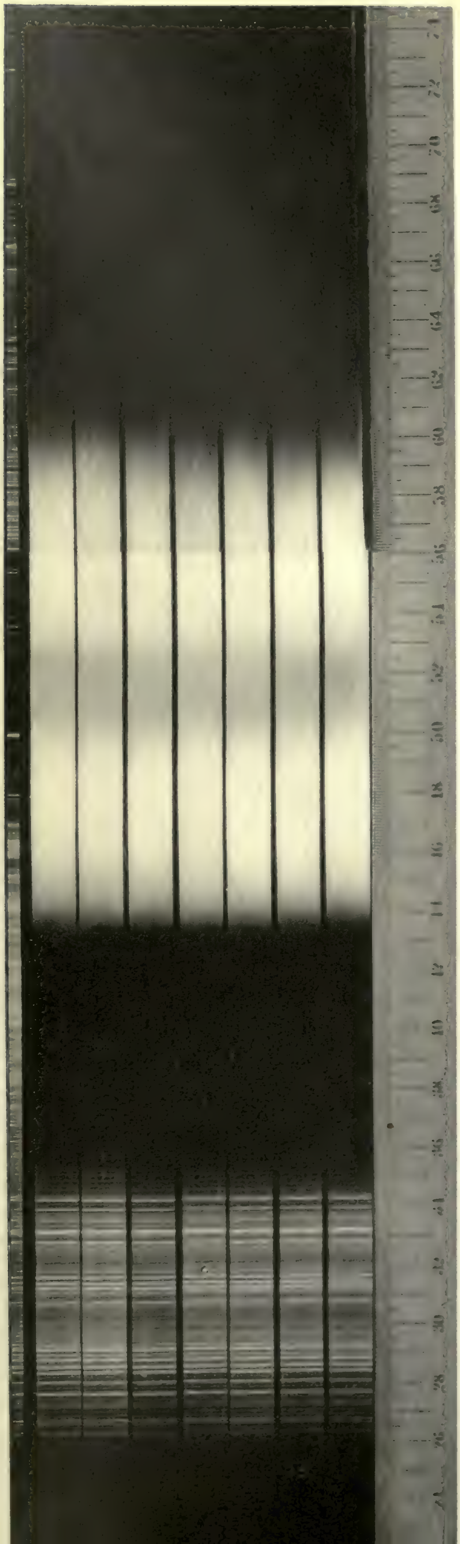

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34

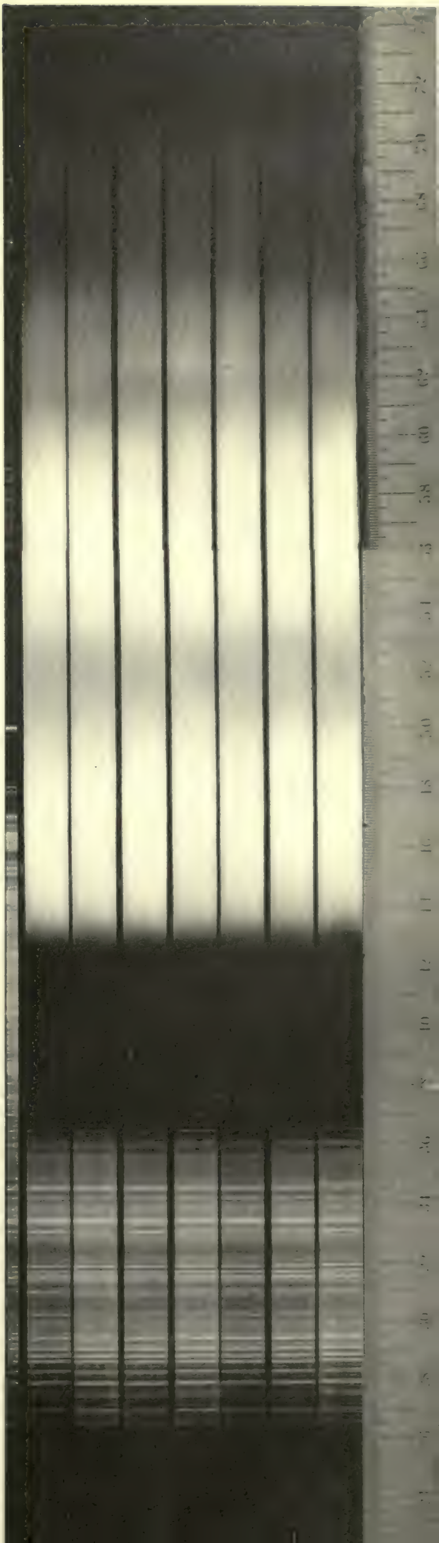
PLATE 27

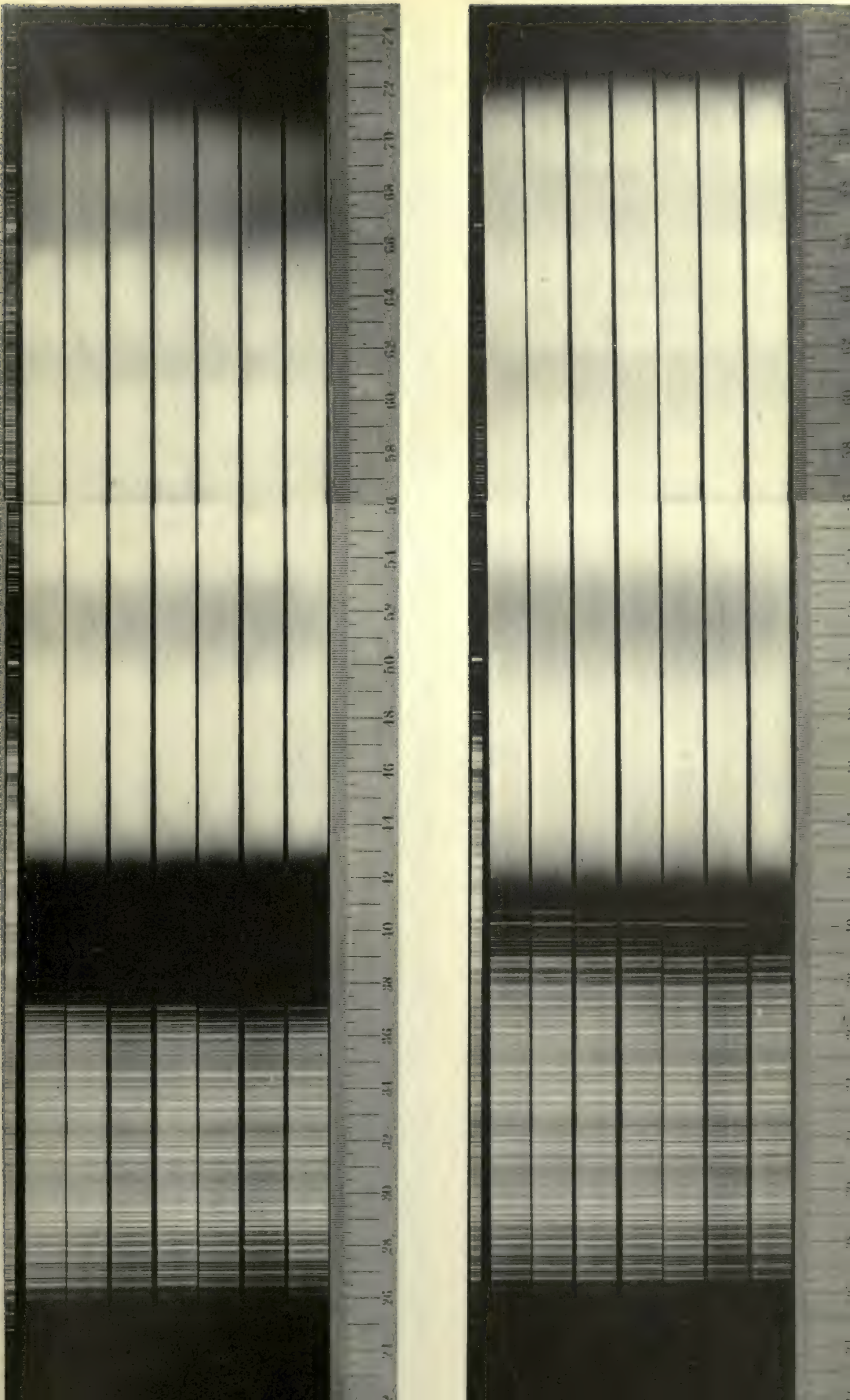

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

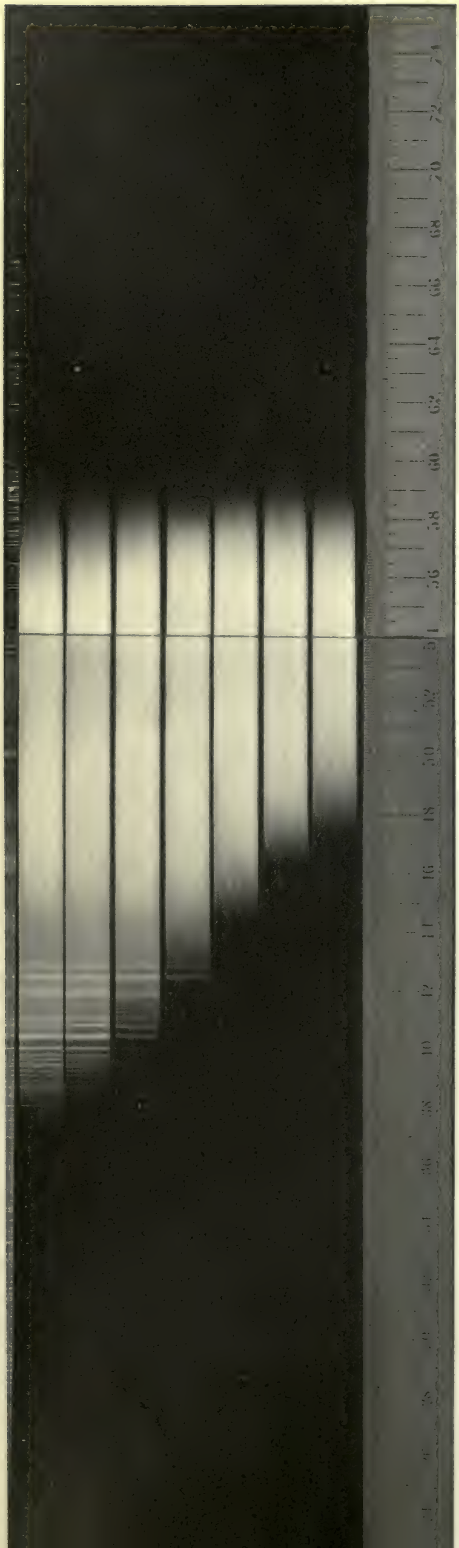
PLAT

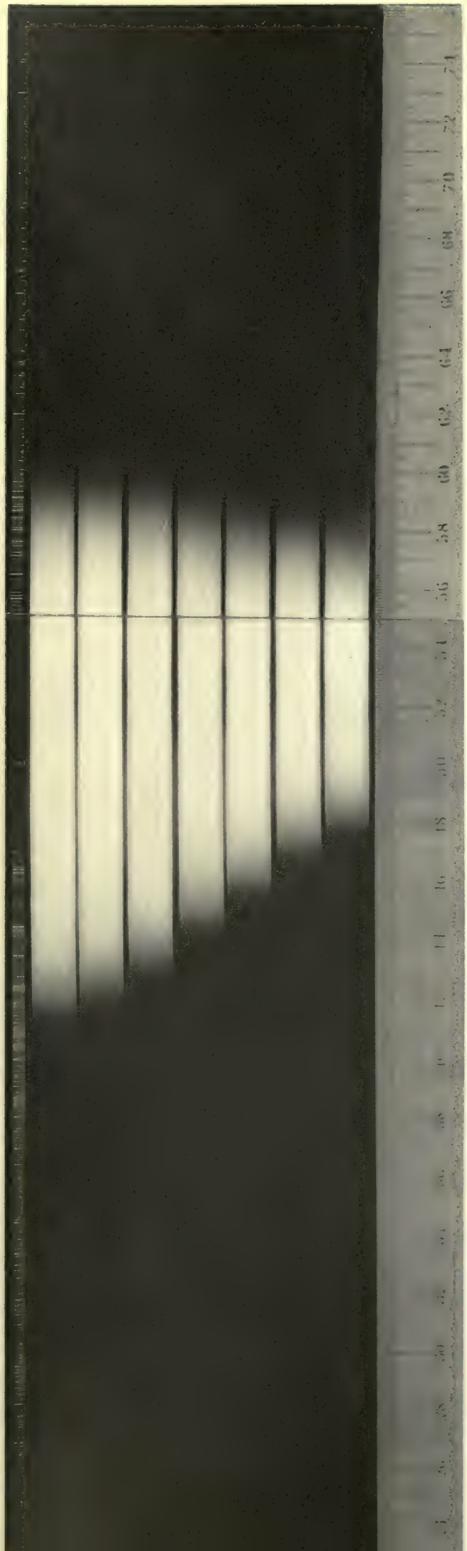


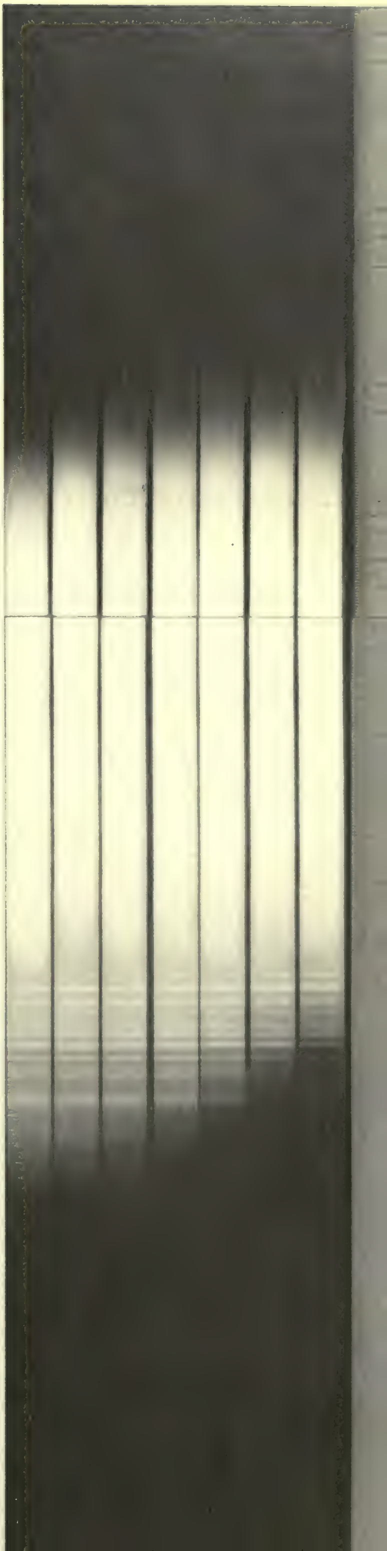
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

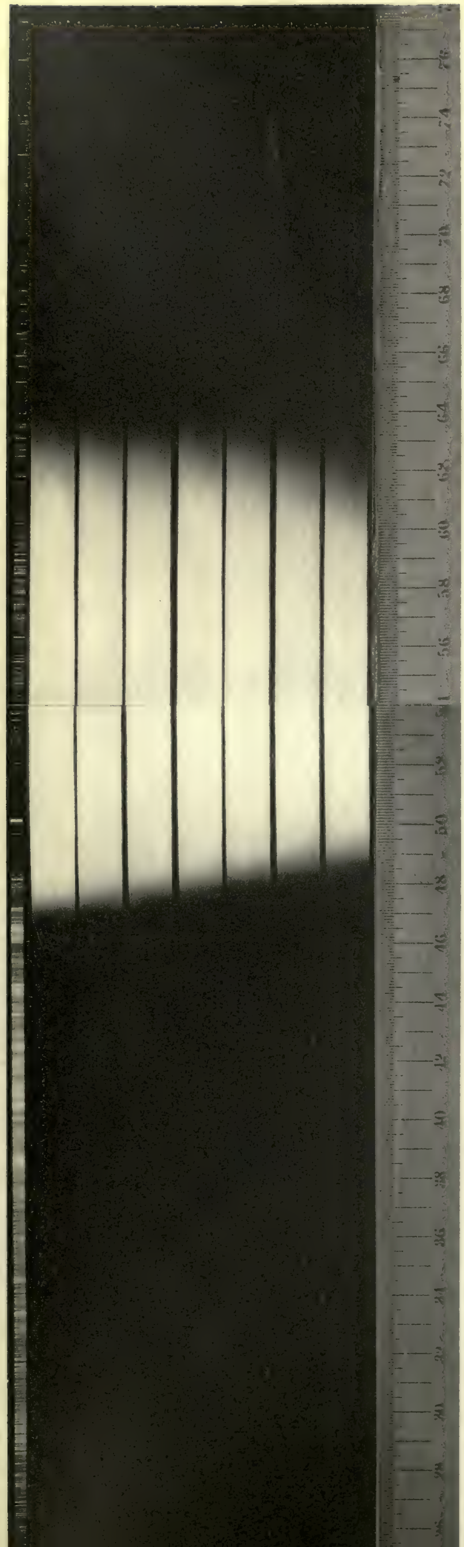


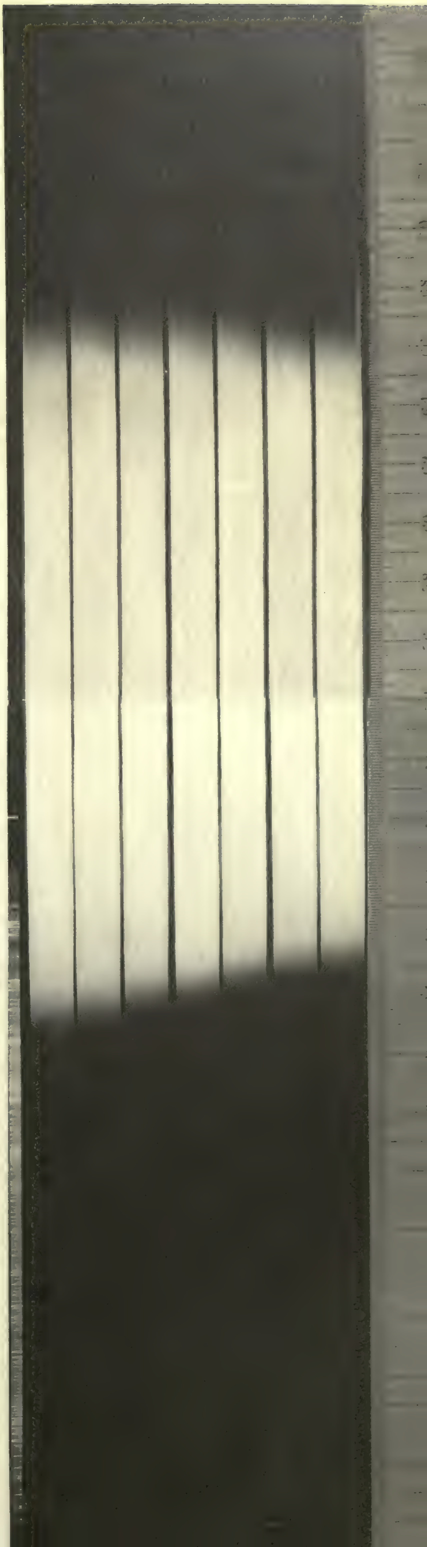

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

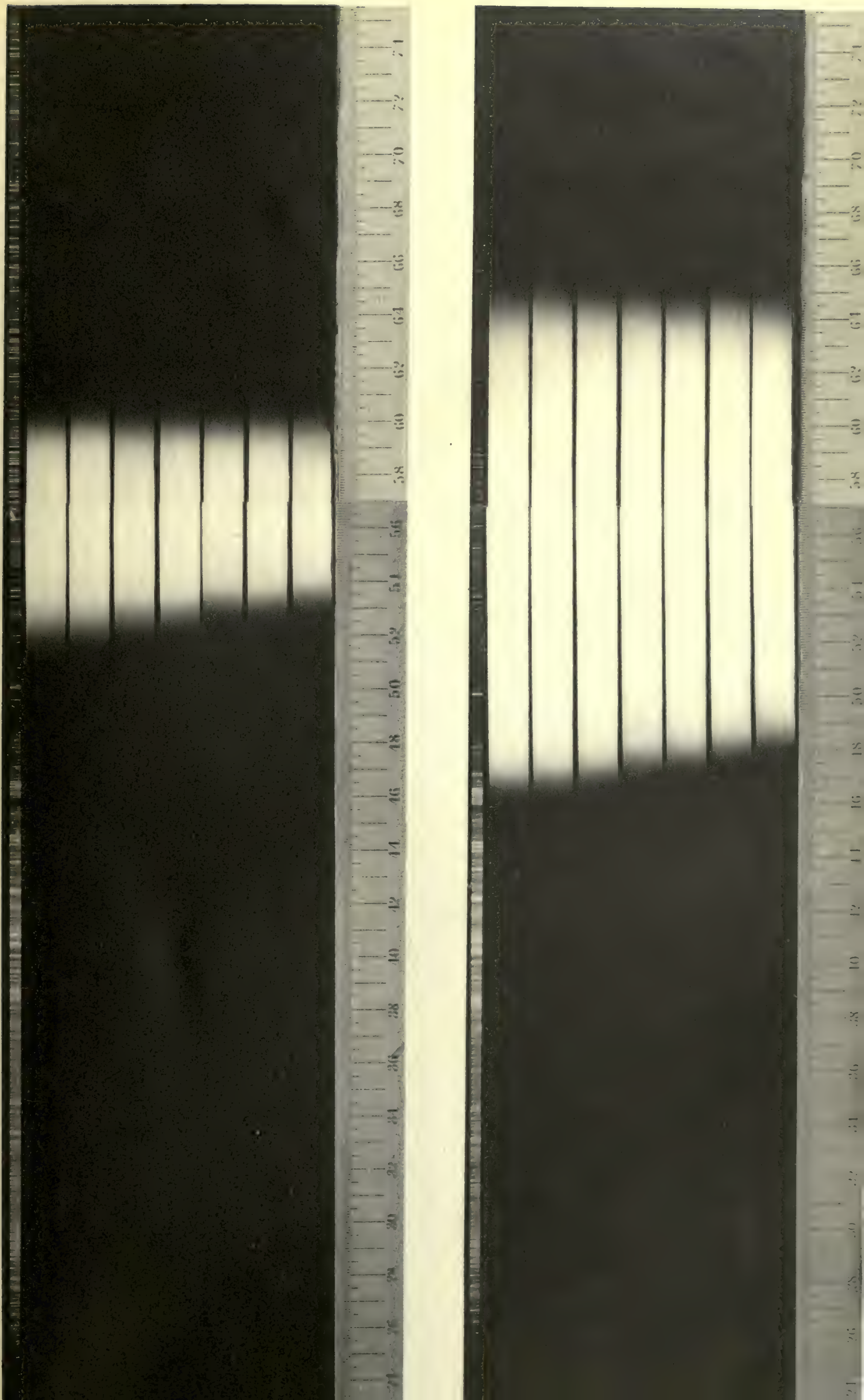

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36

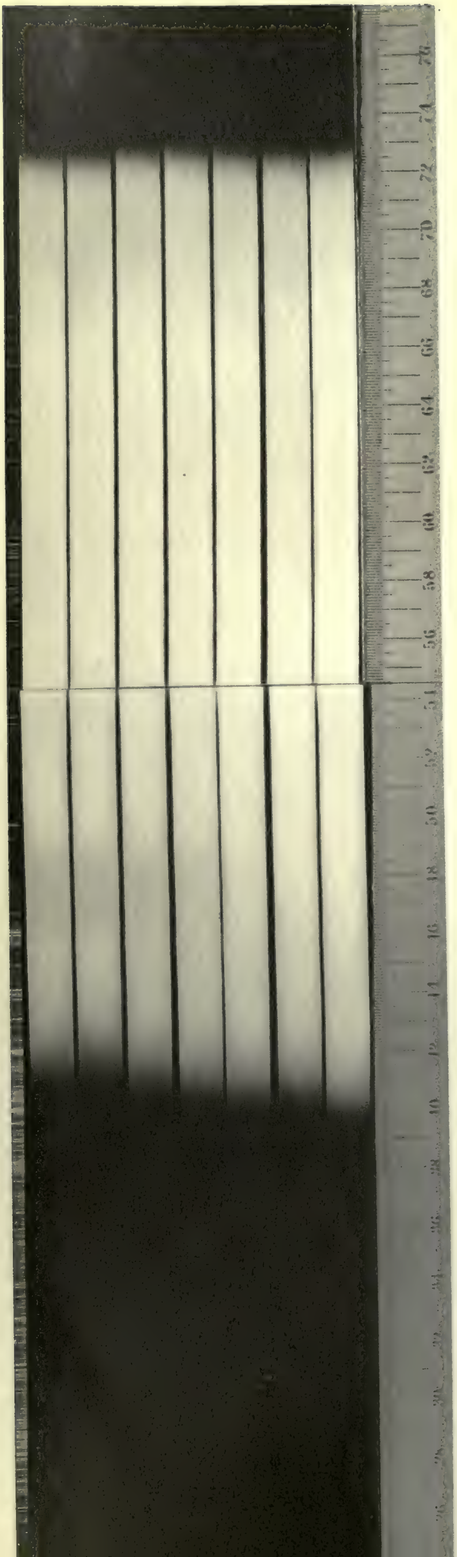

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44

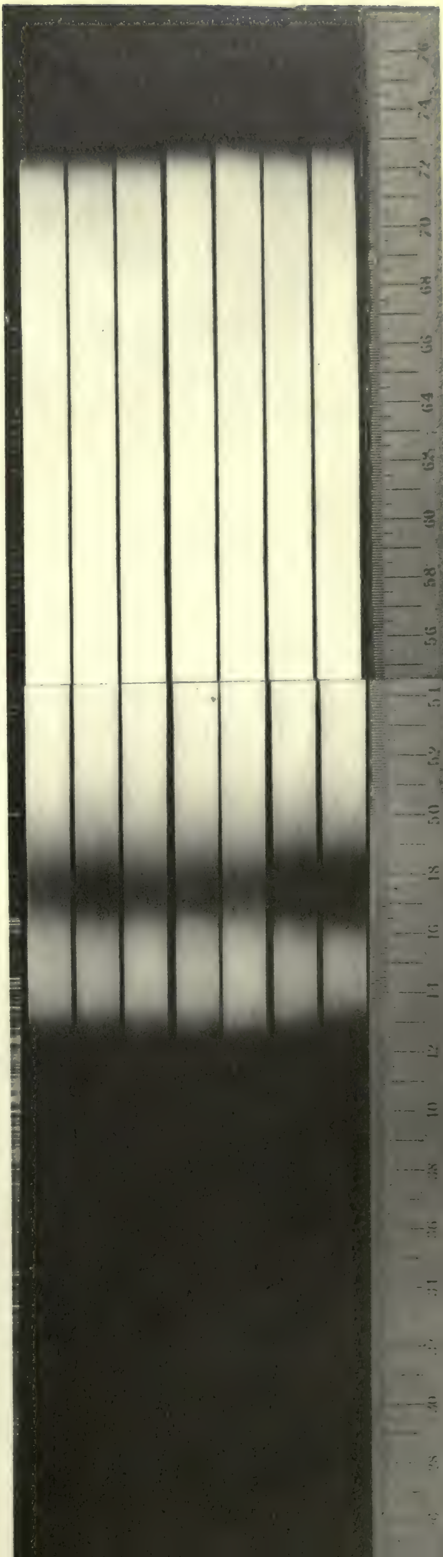


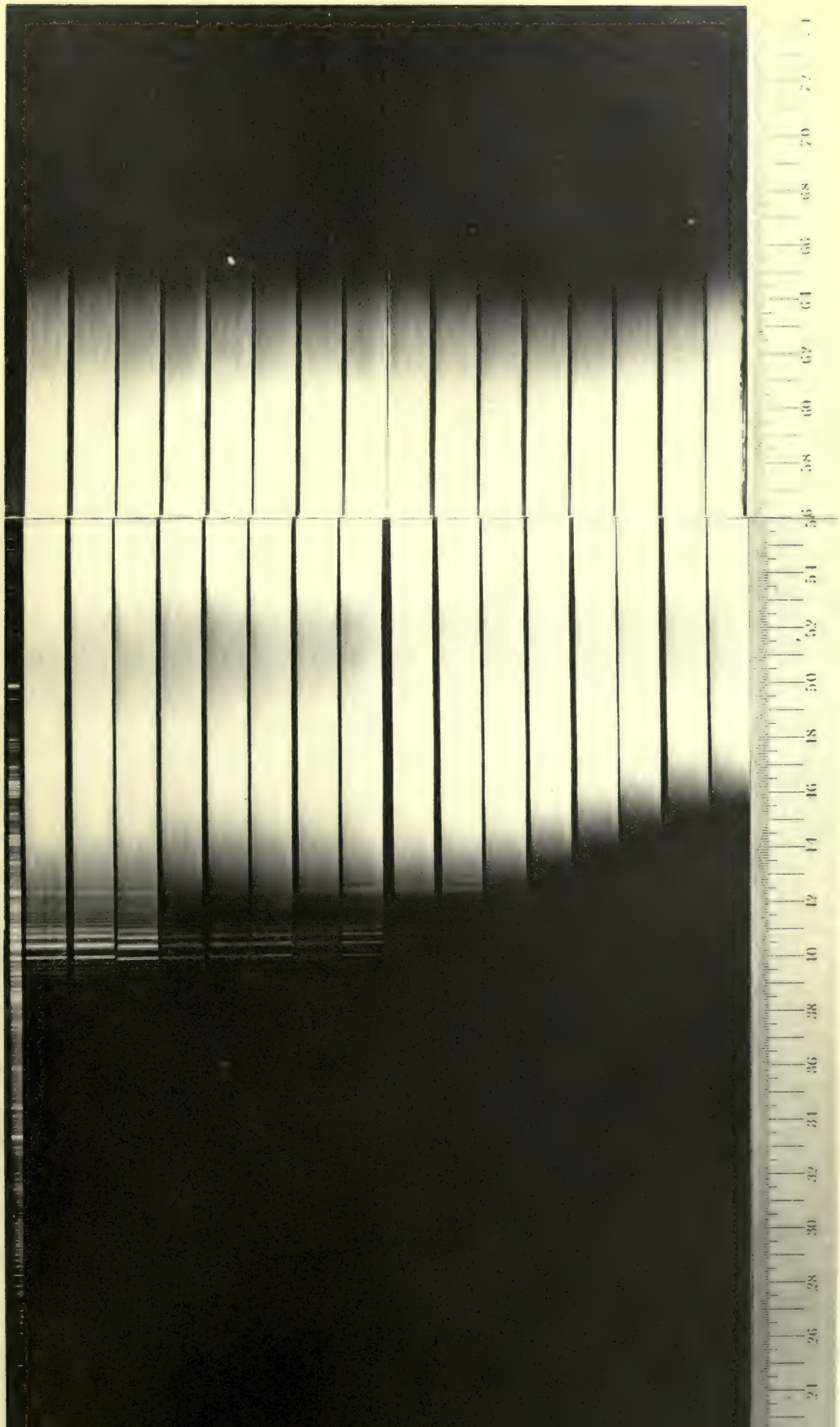

76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28

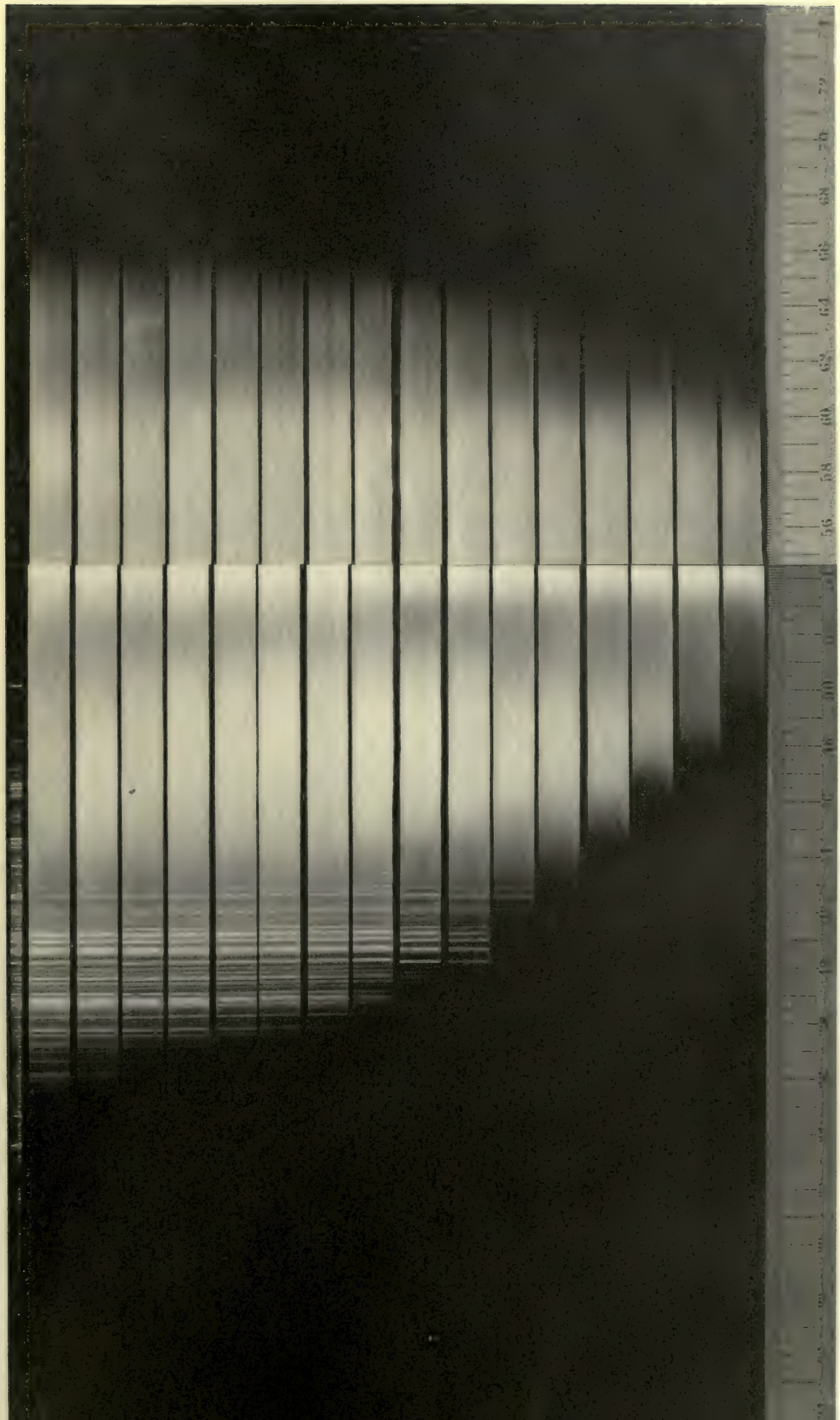


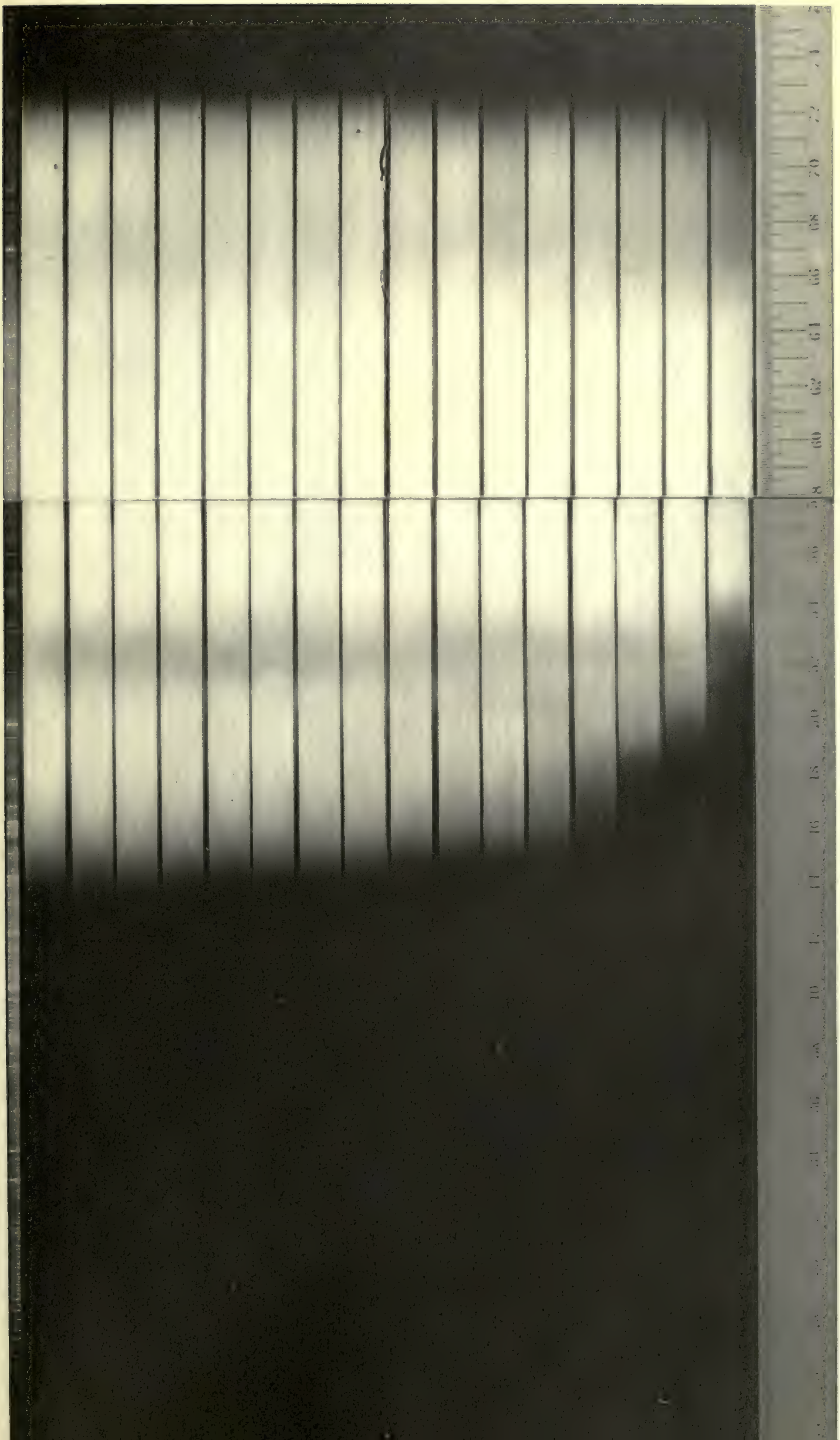

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

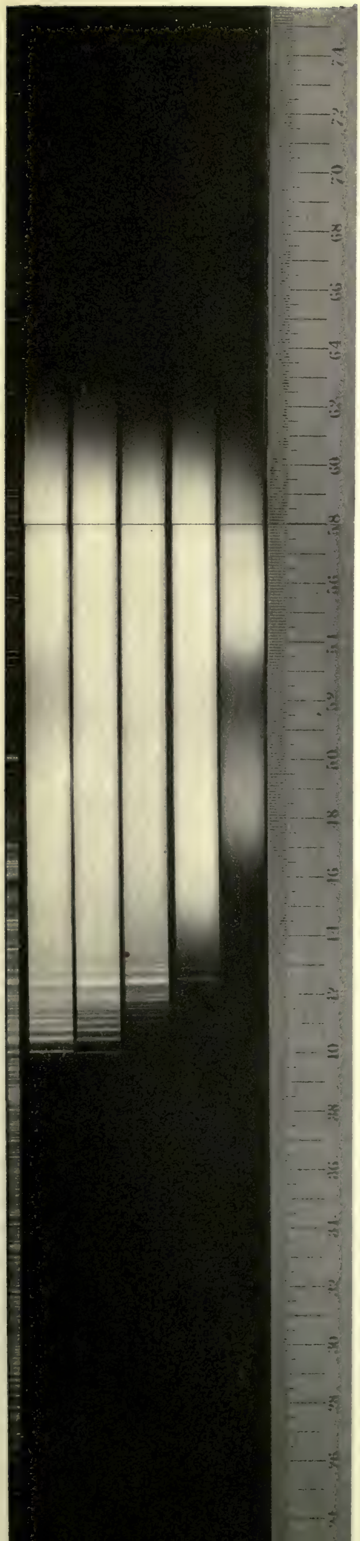

76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26


76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

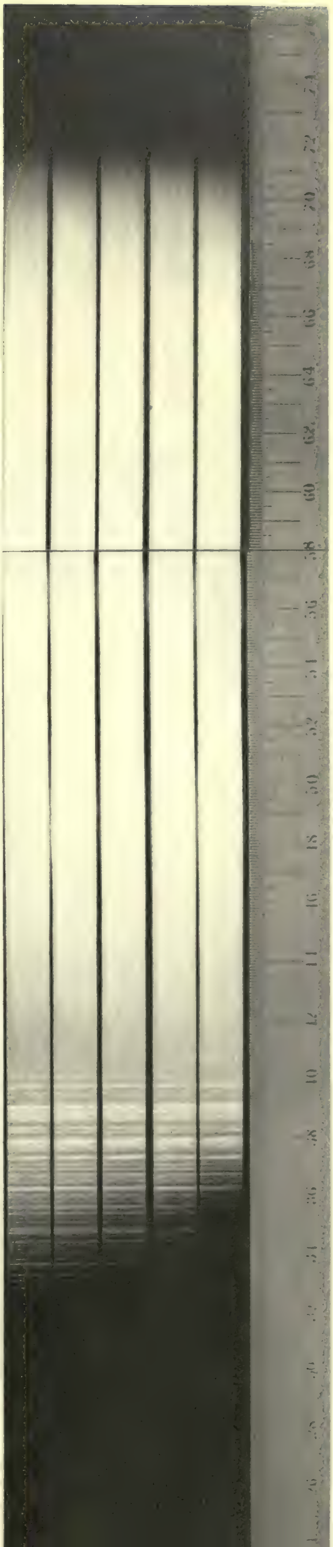

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24


56
58
60
62
64
66
68
70
72

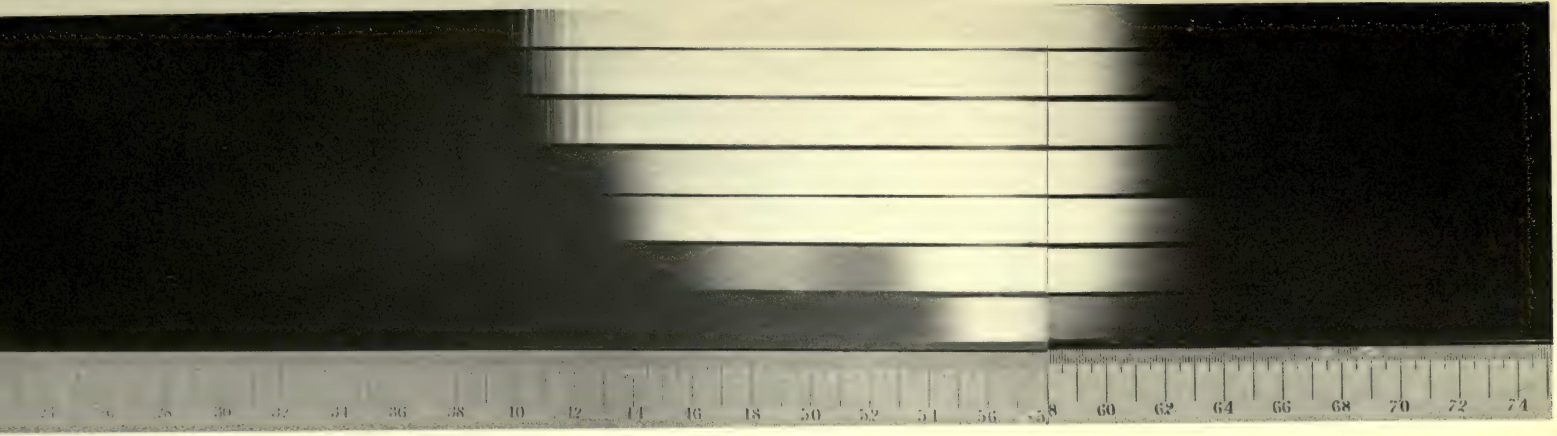




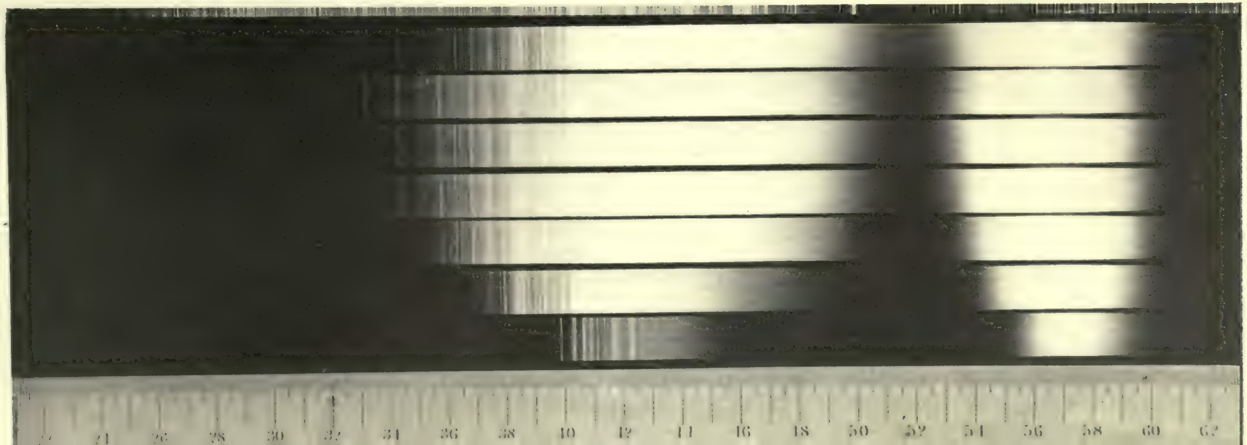
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

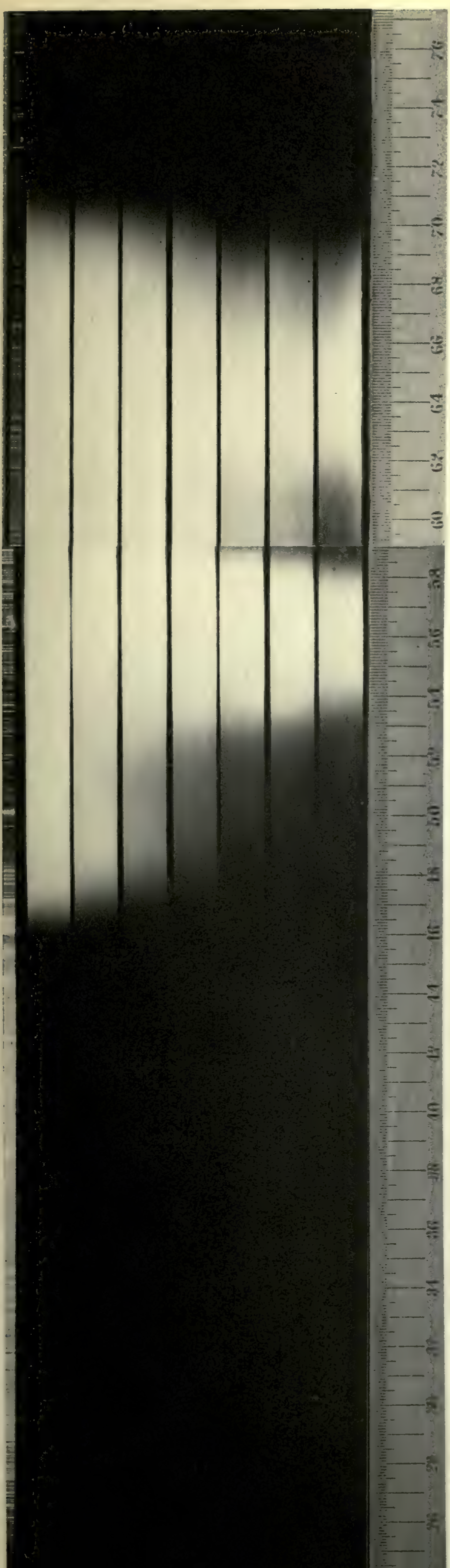


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24


26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72
74

B


24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62


76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

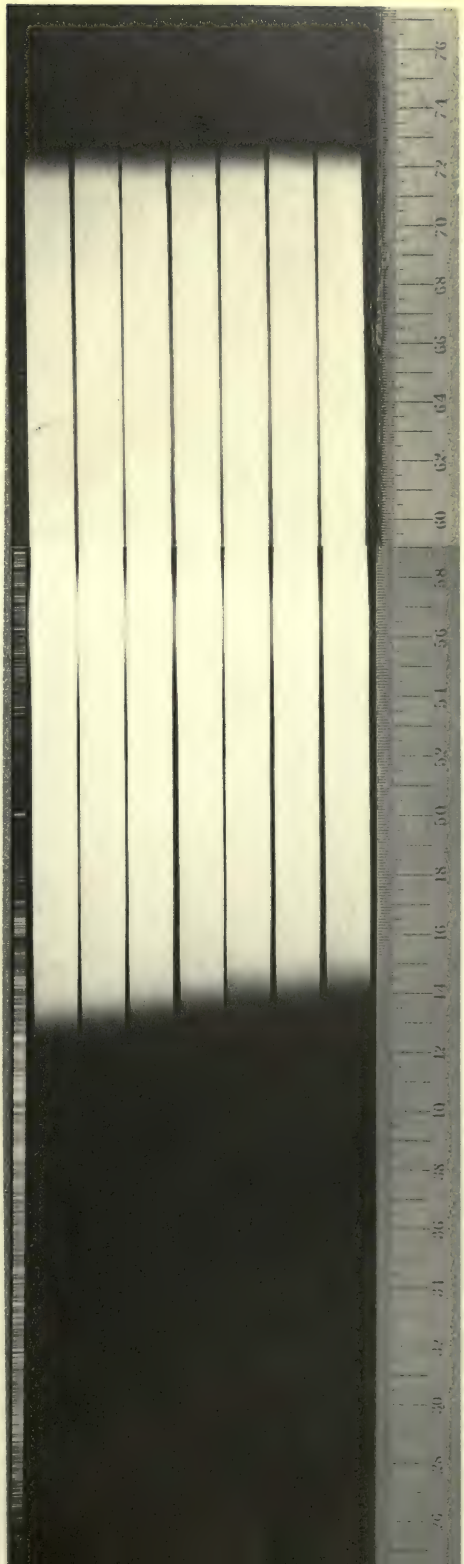
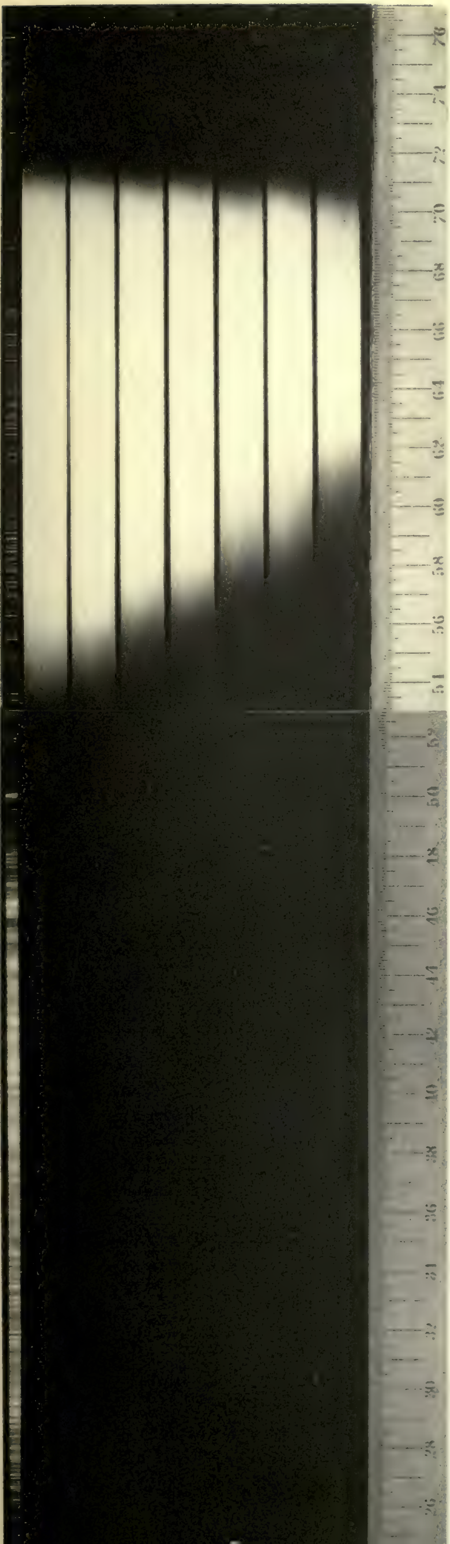
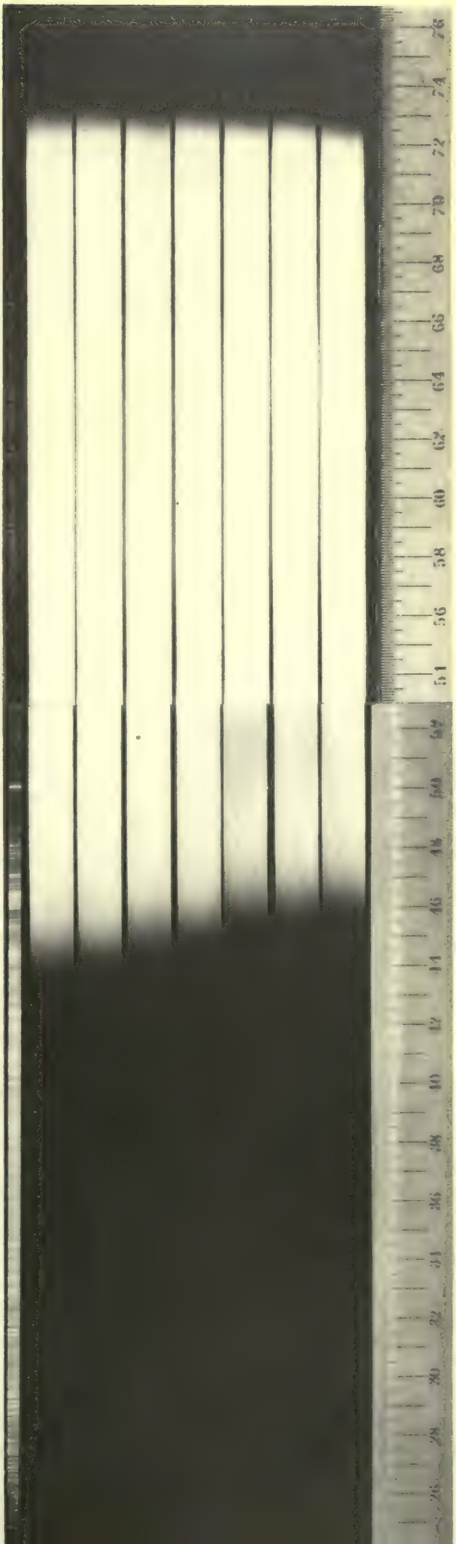
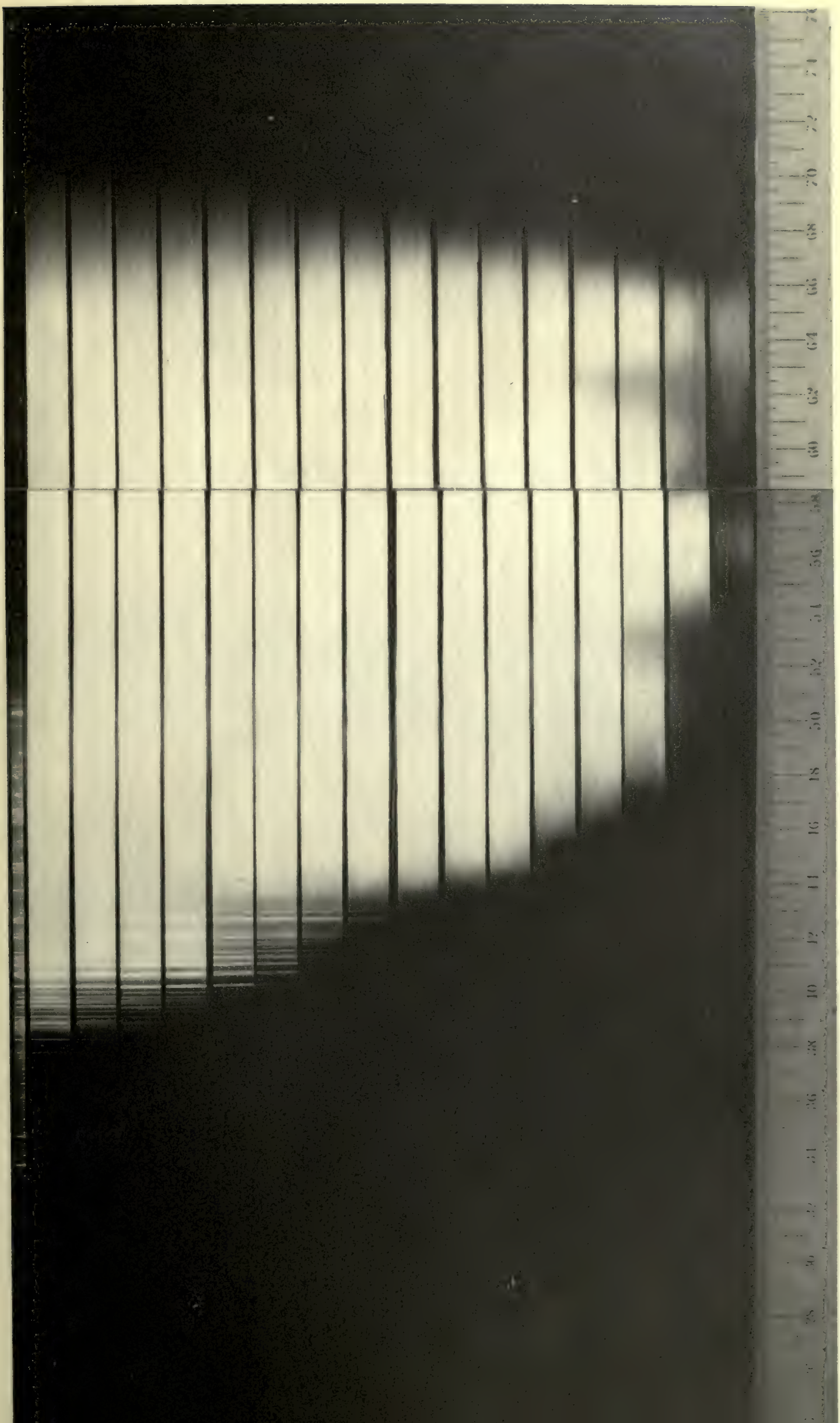

76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

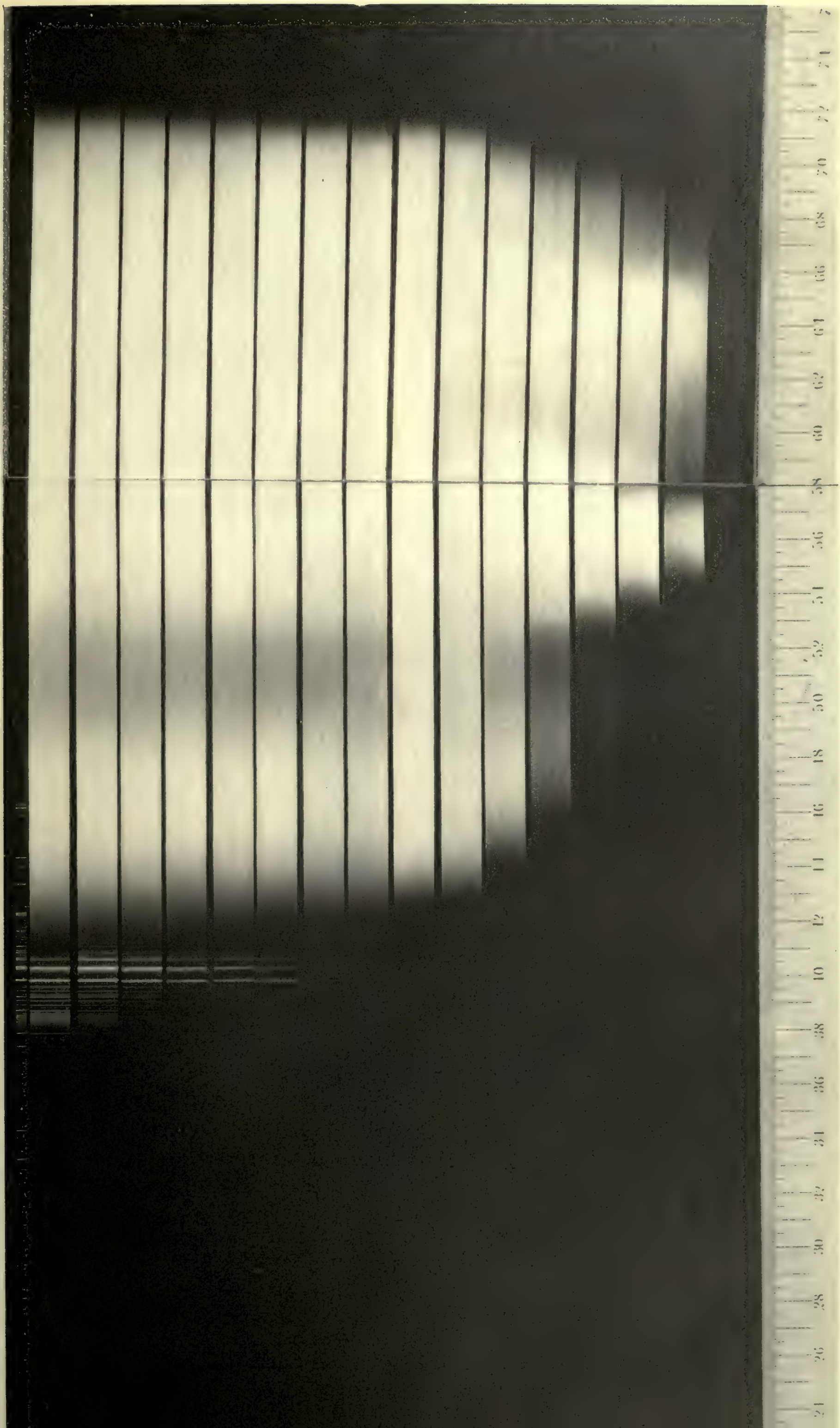
PLATE 41


76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

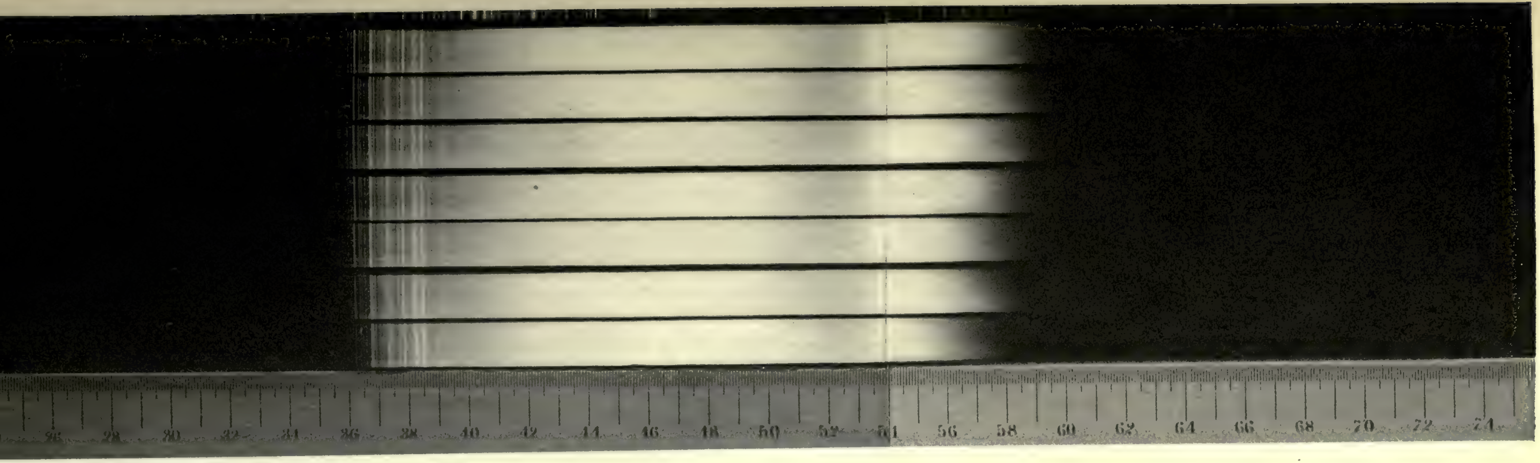

76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

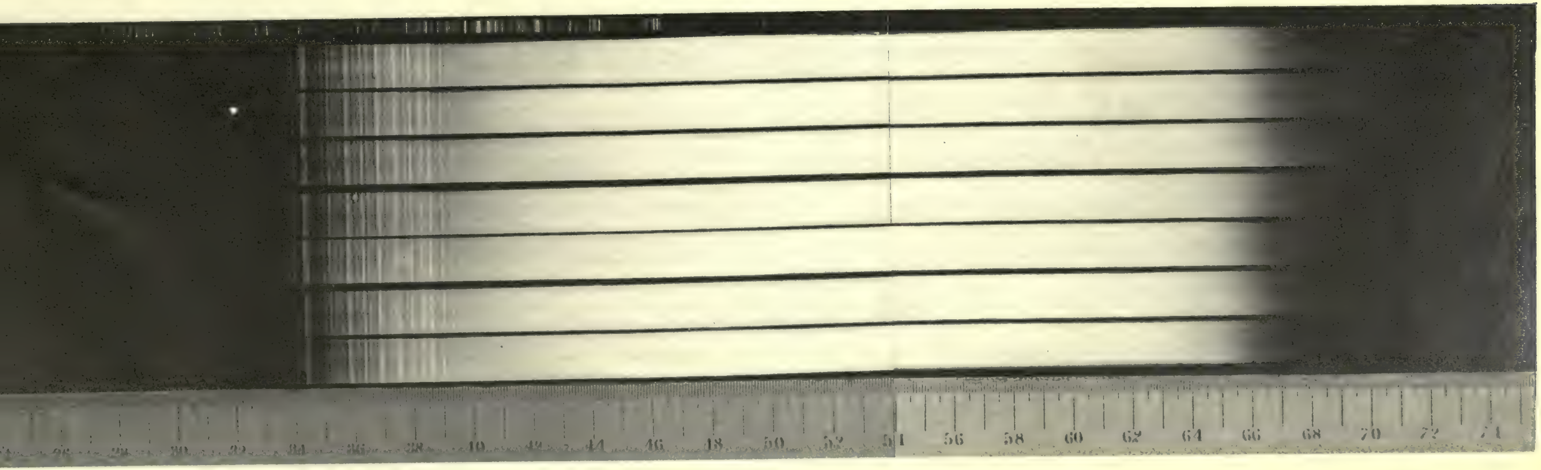

70
68
66
64
62
60
58
56
54
52
50
48

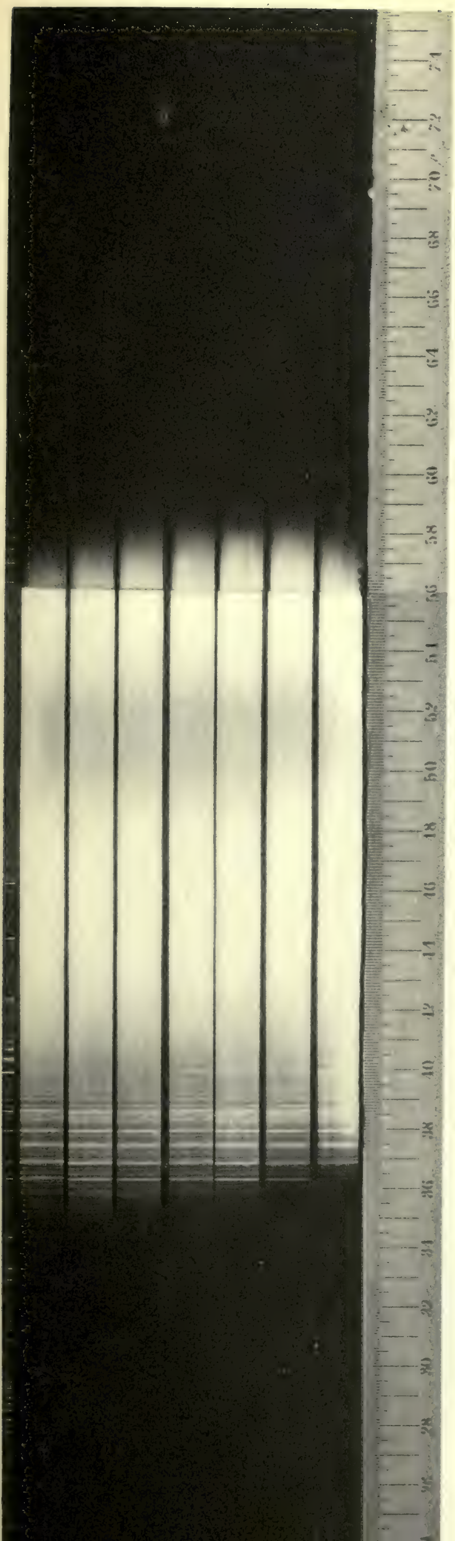
PLATE

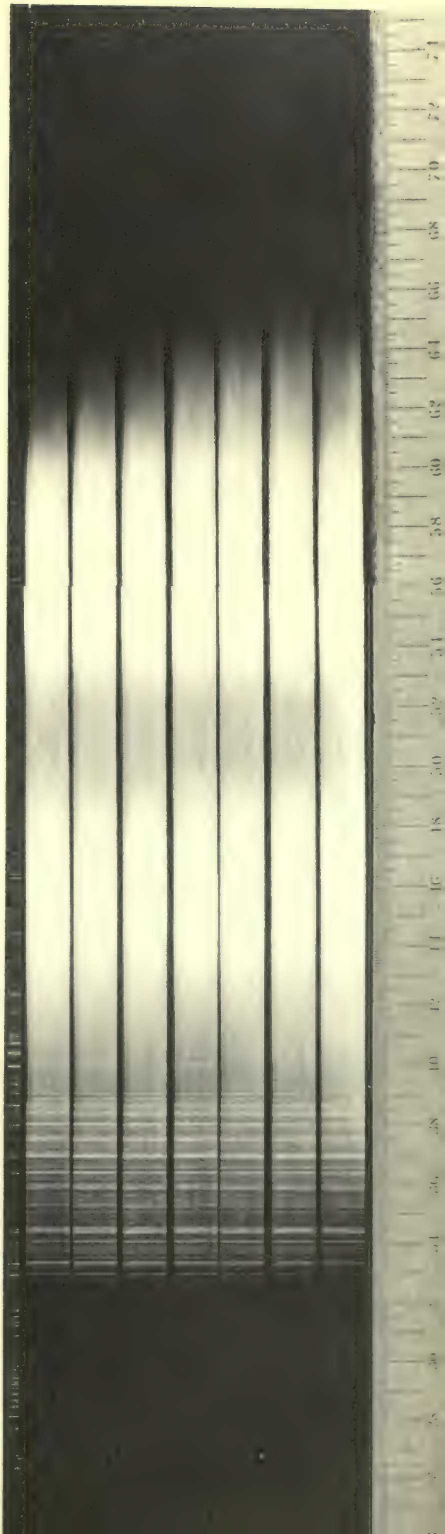


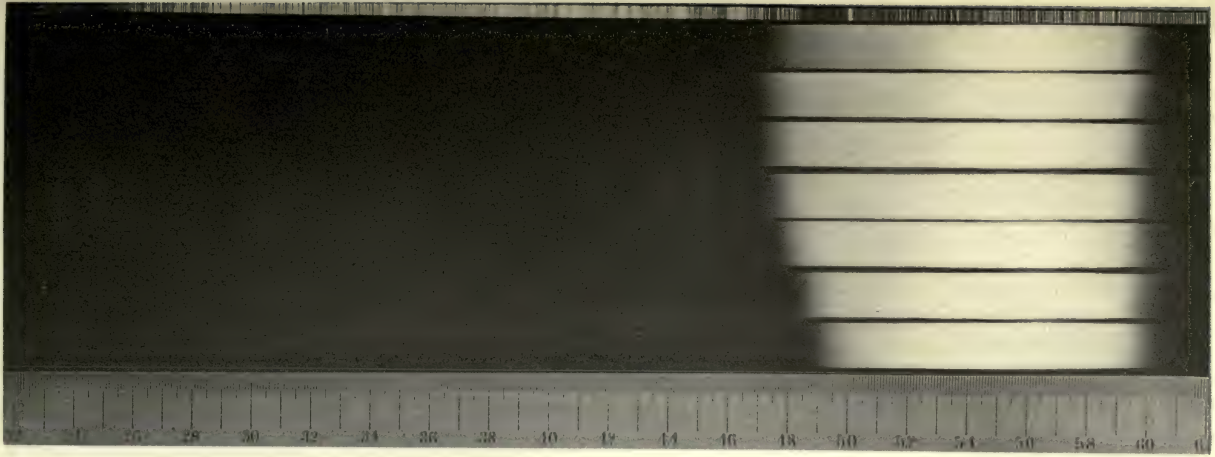
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24


26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72
74

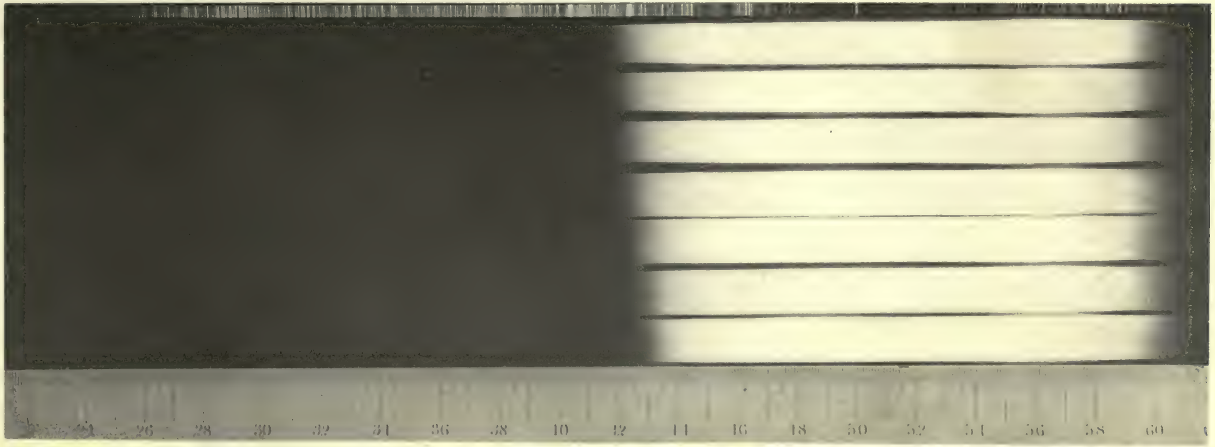

26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72
74


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

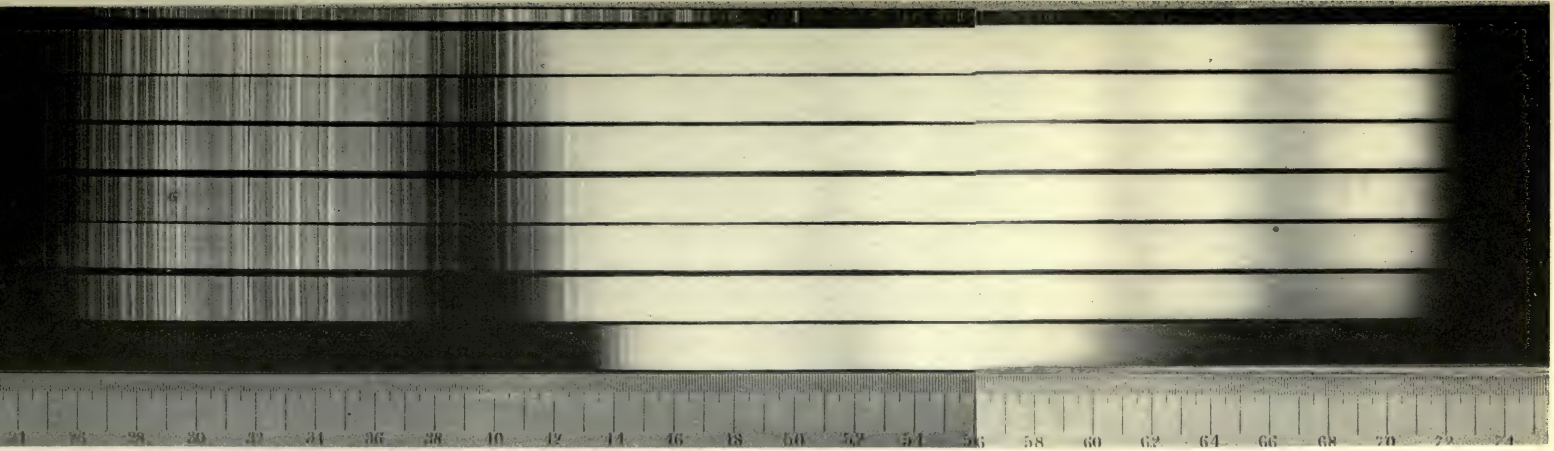

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
30
28

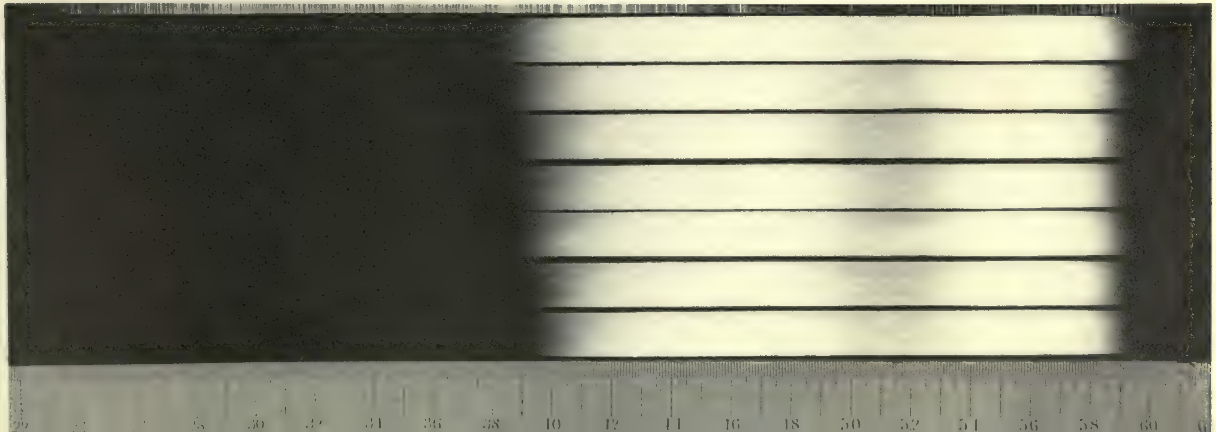

24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60

A


24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60

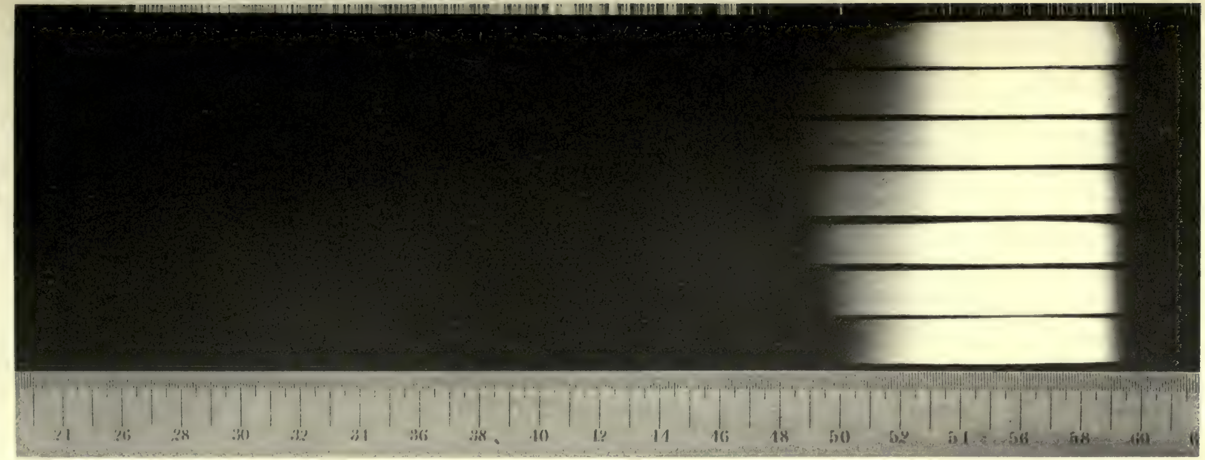
B


24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72
74

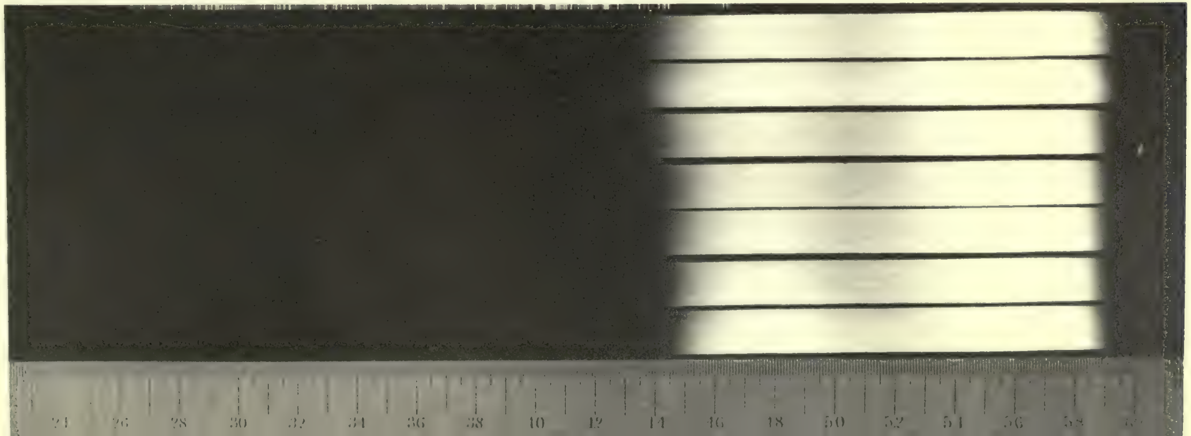

30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

B

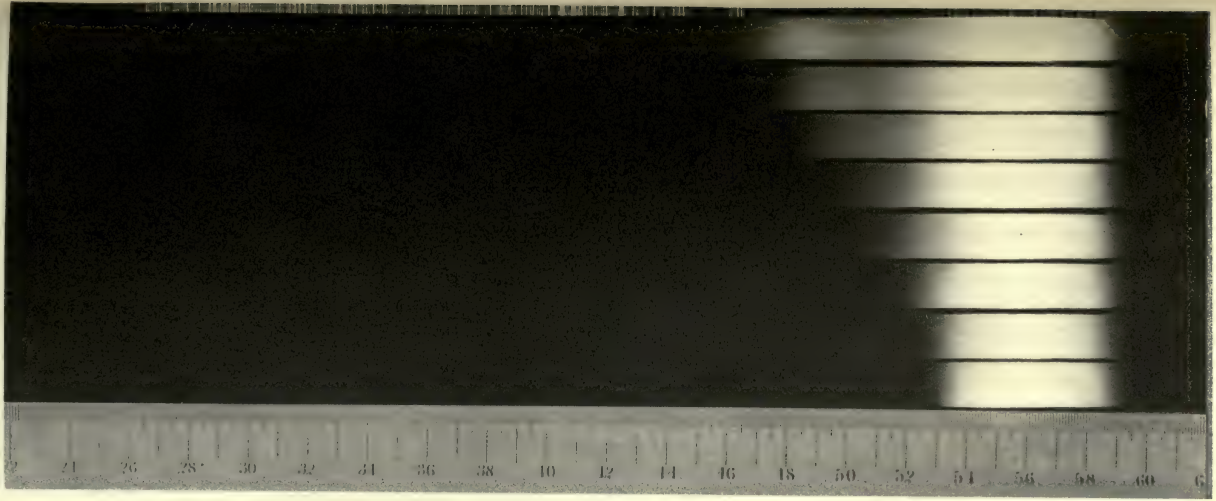
A


24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

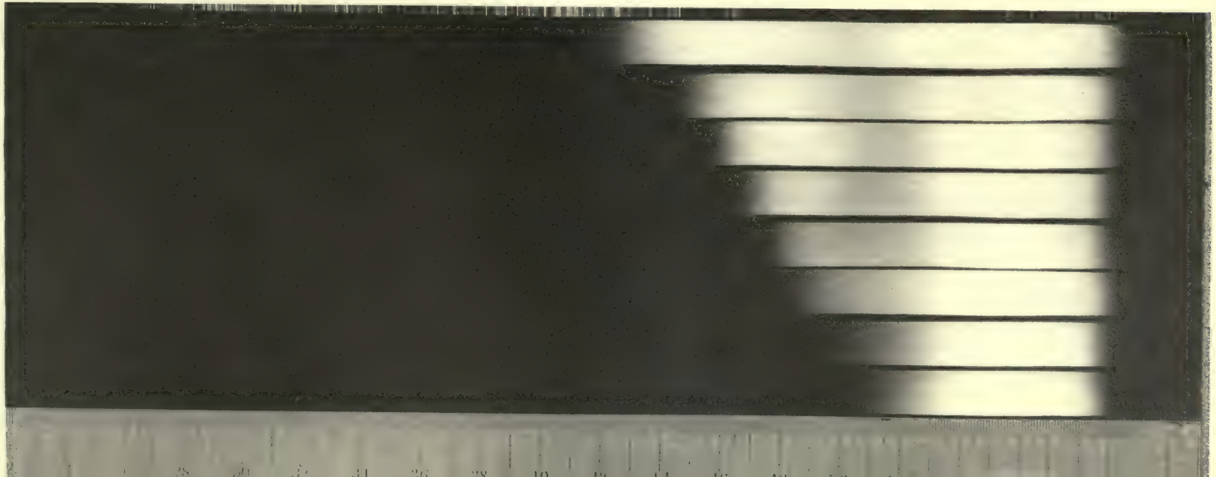
B

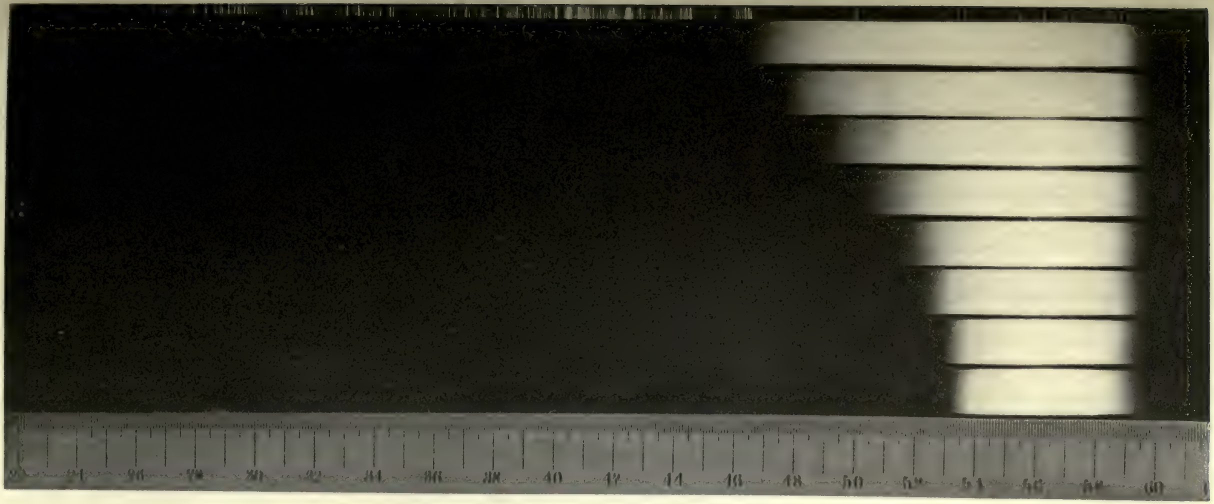

24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58

A

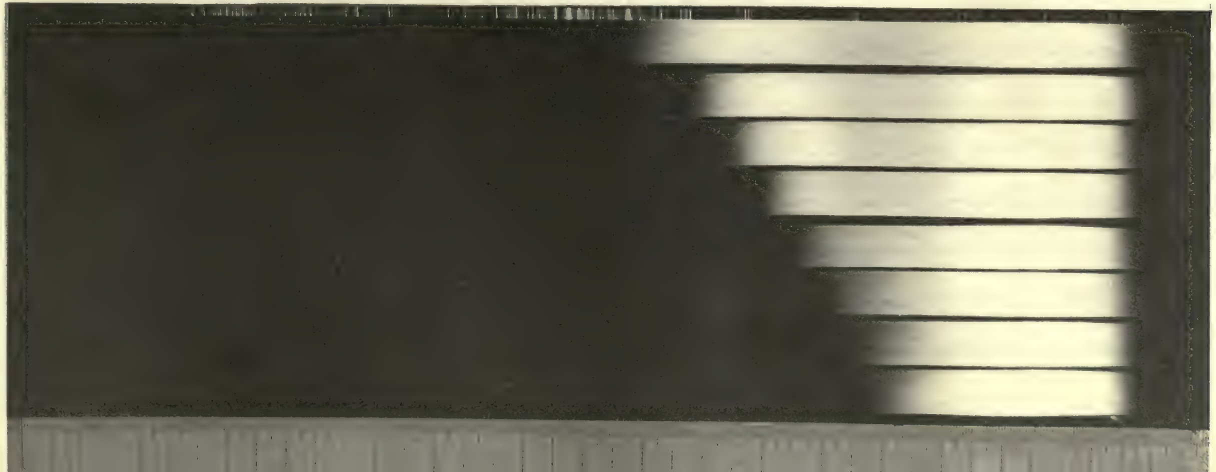

24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

B



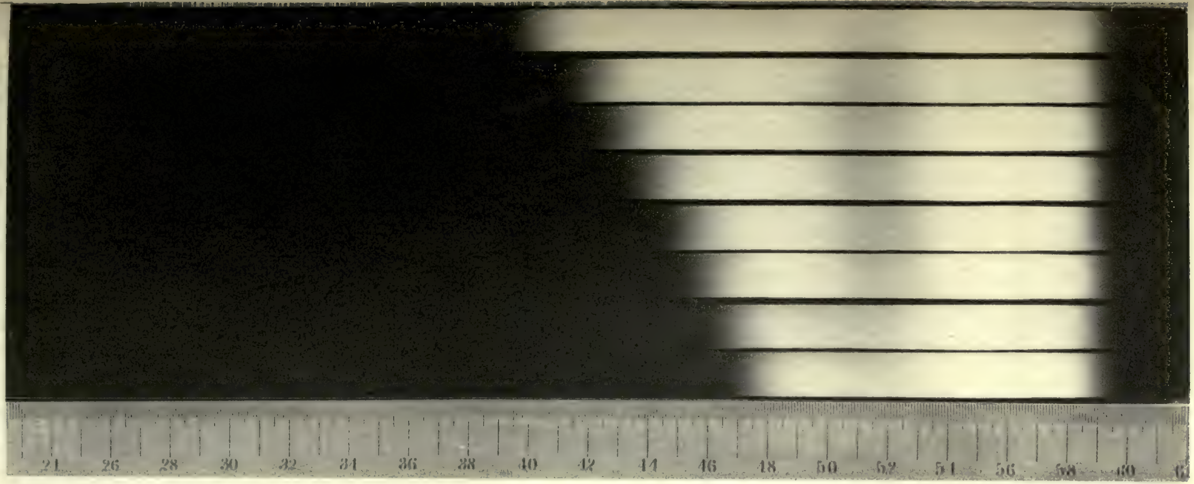

24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

A

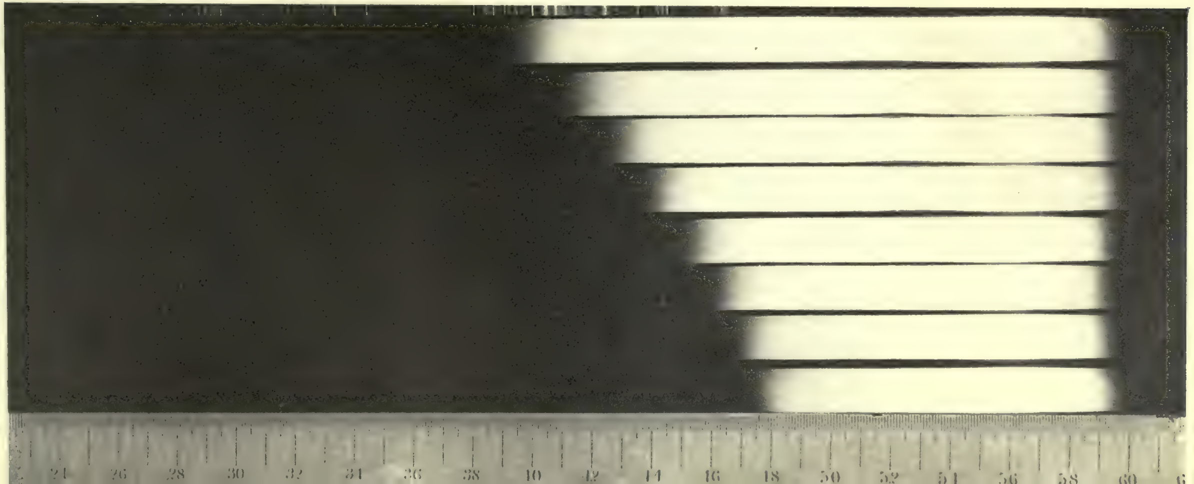


B

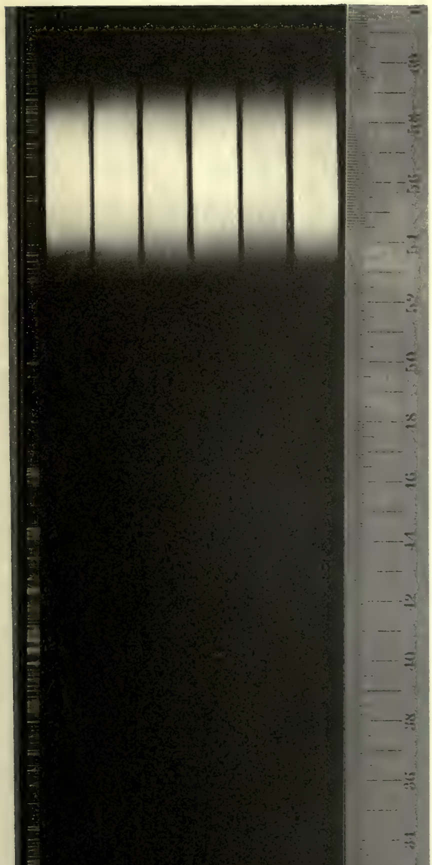
A


24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

B

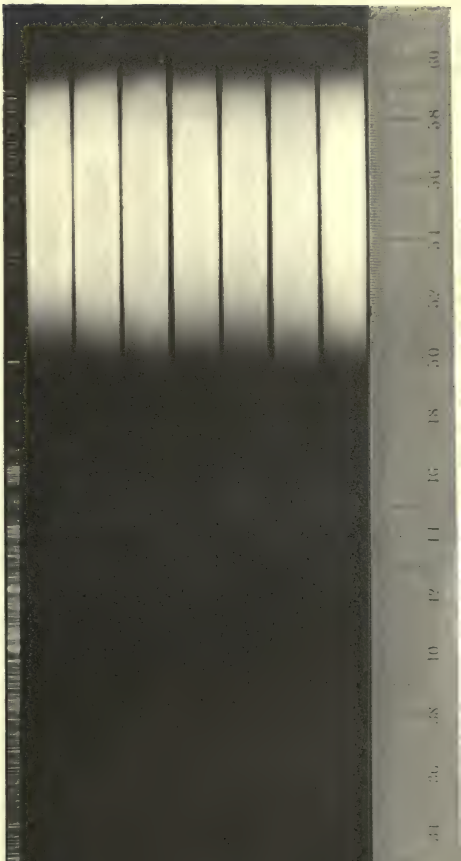

24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

PLAT



24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

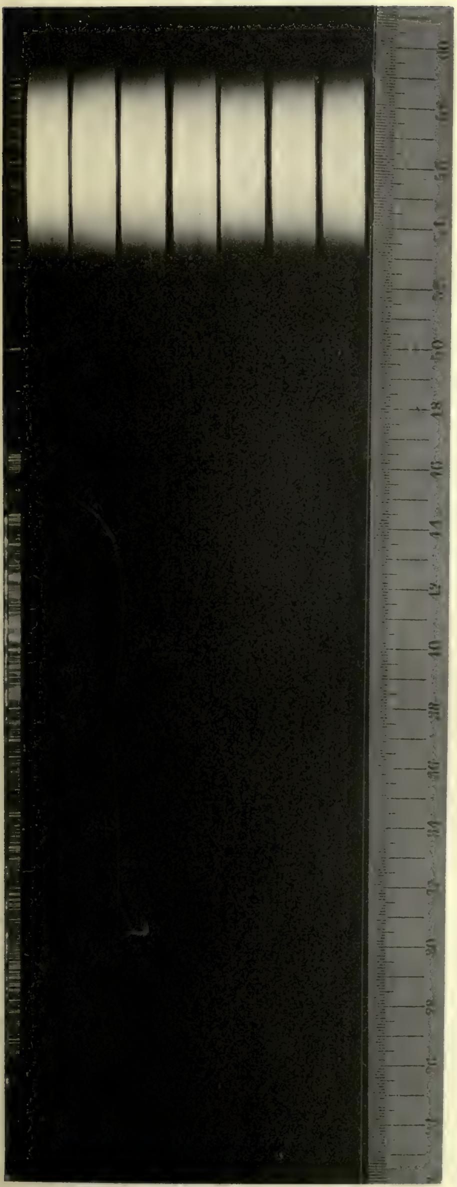
A



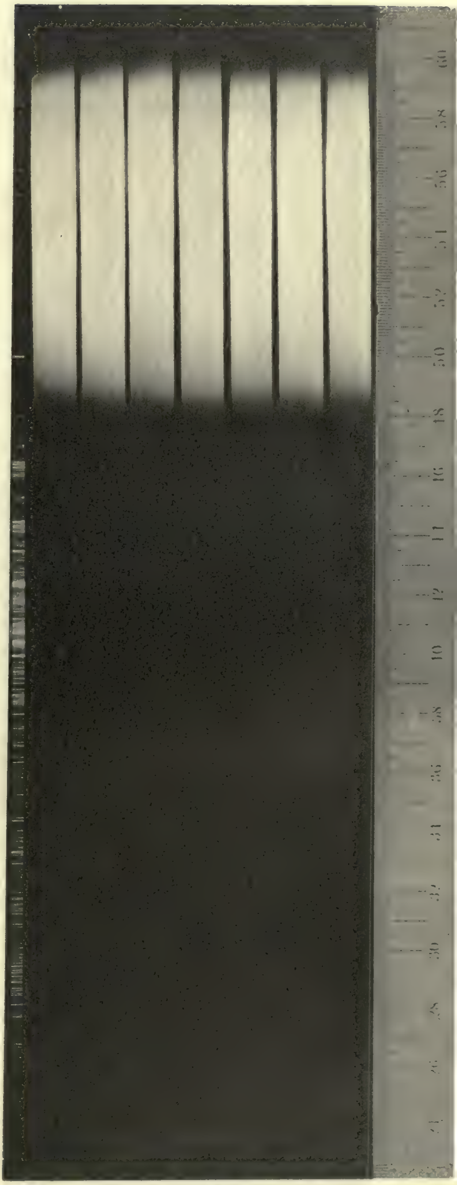
10
12
14
16
18
50
52
54
56
58
60

B

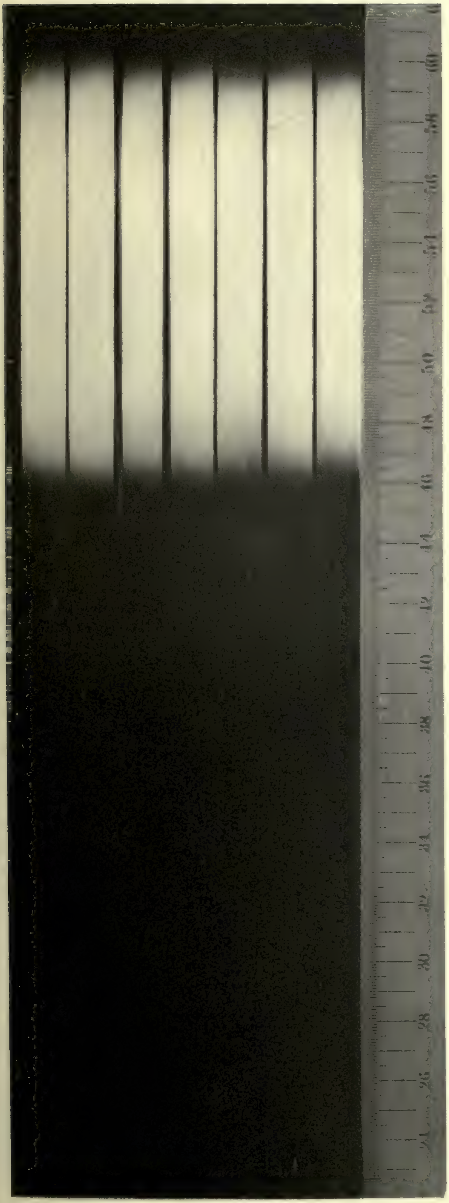
PLA



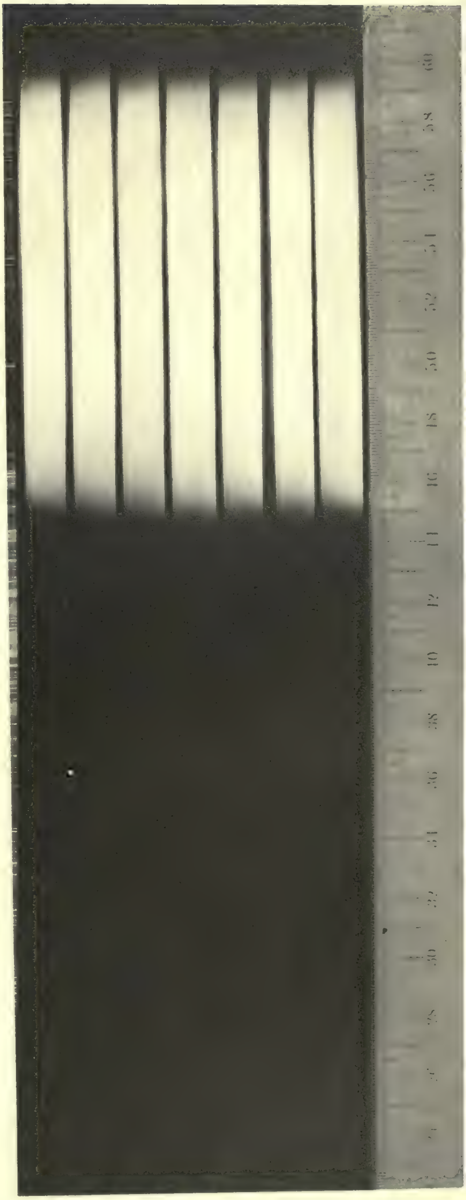
A



B

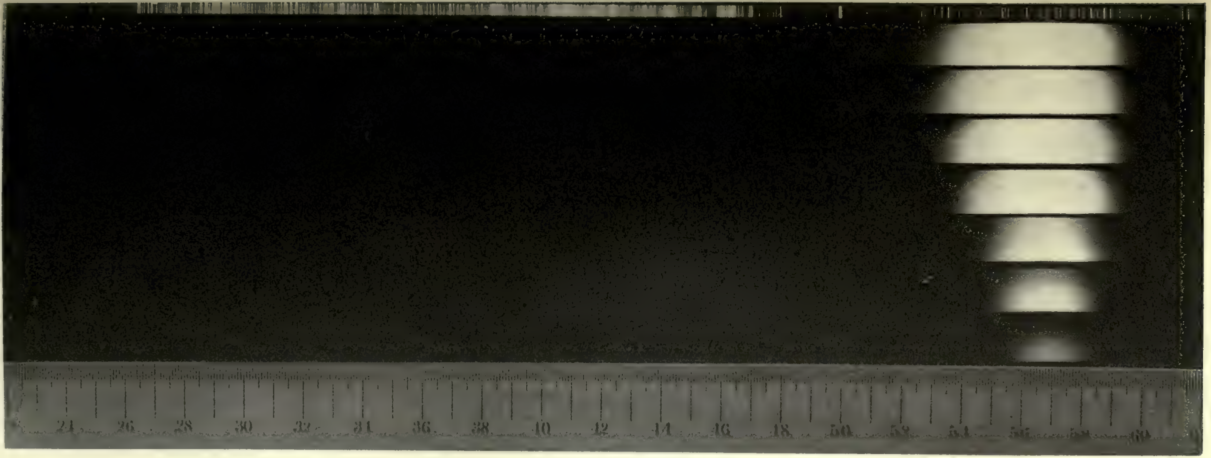


A

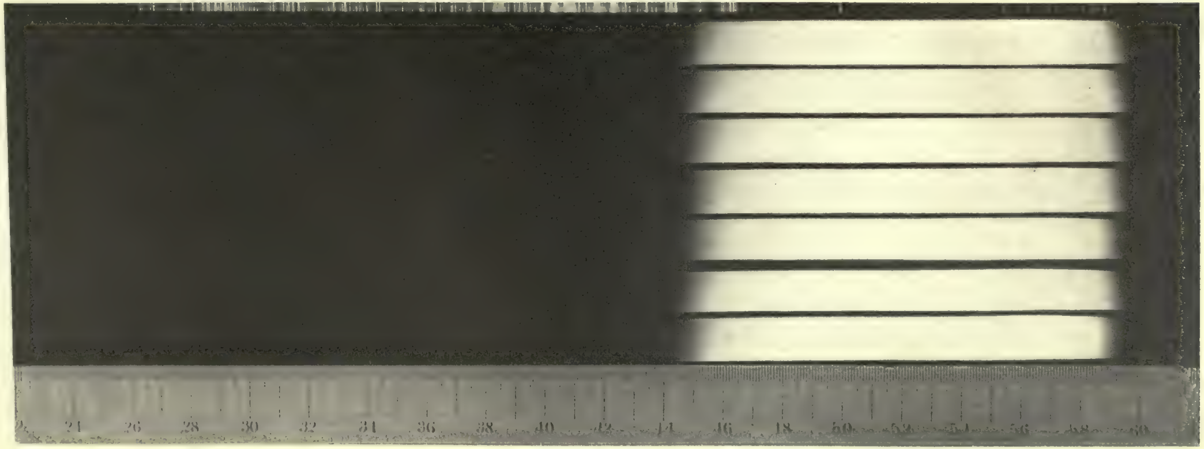


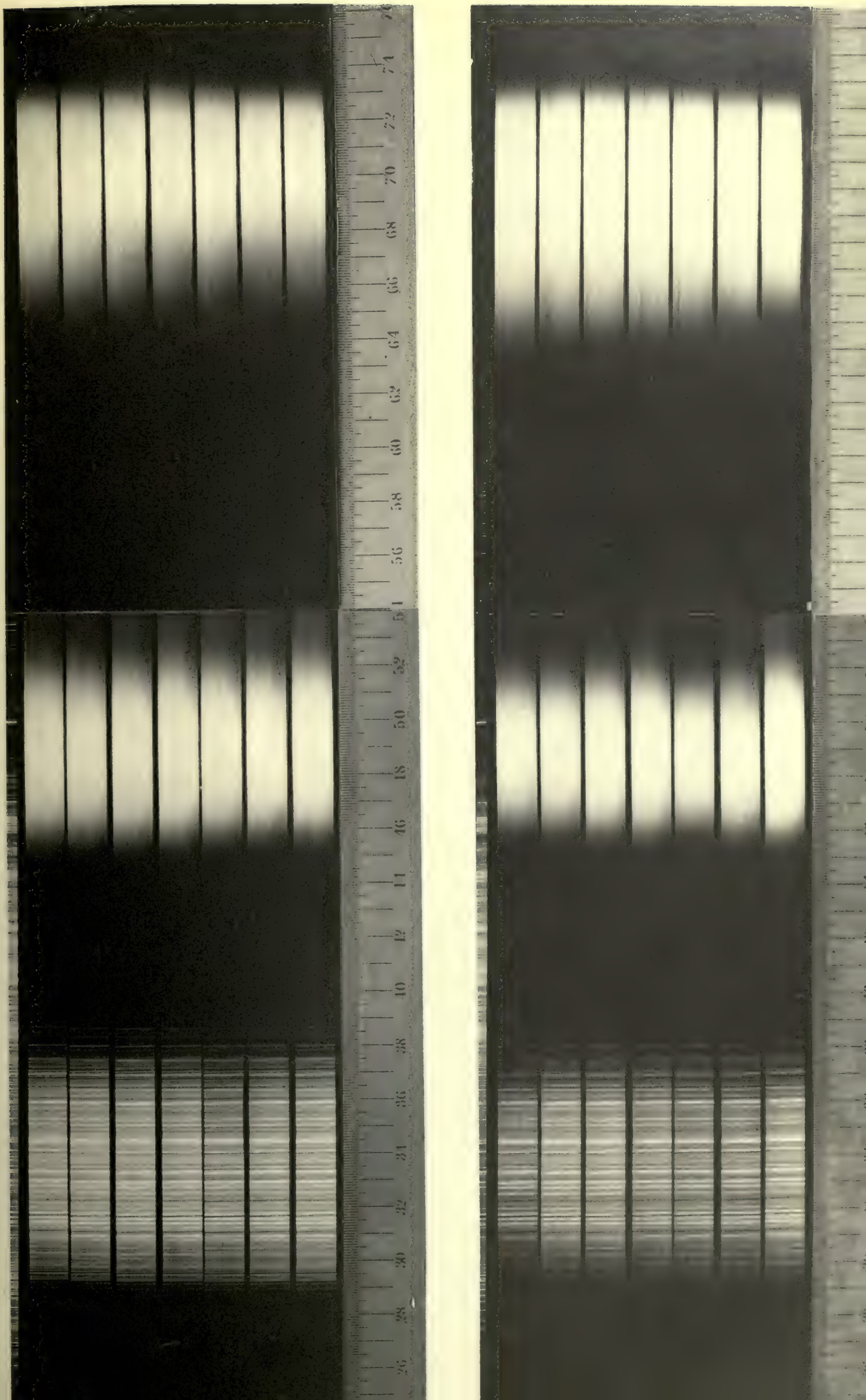
B

A

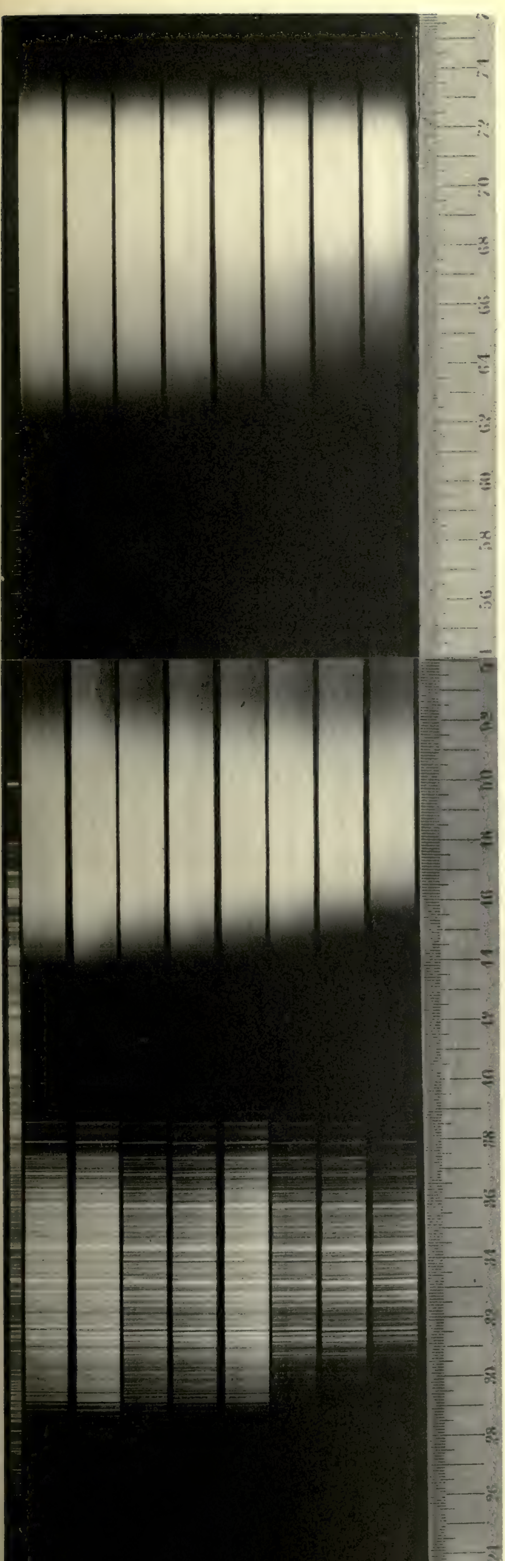

24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

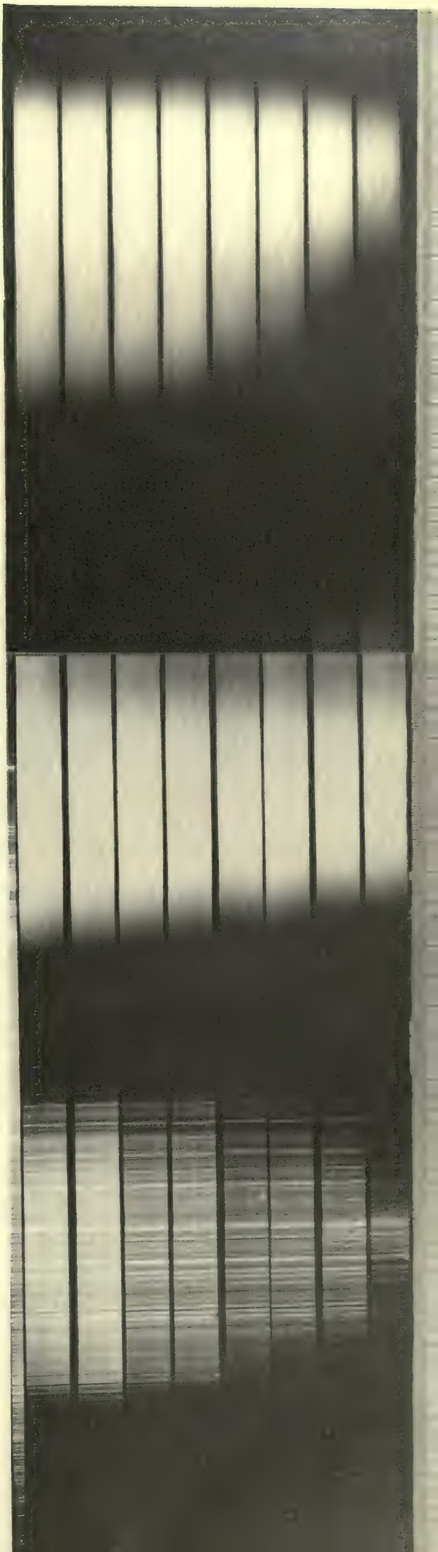
B

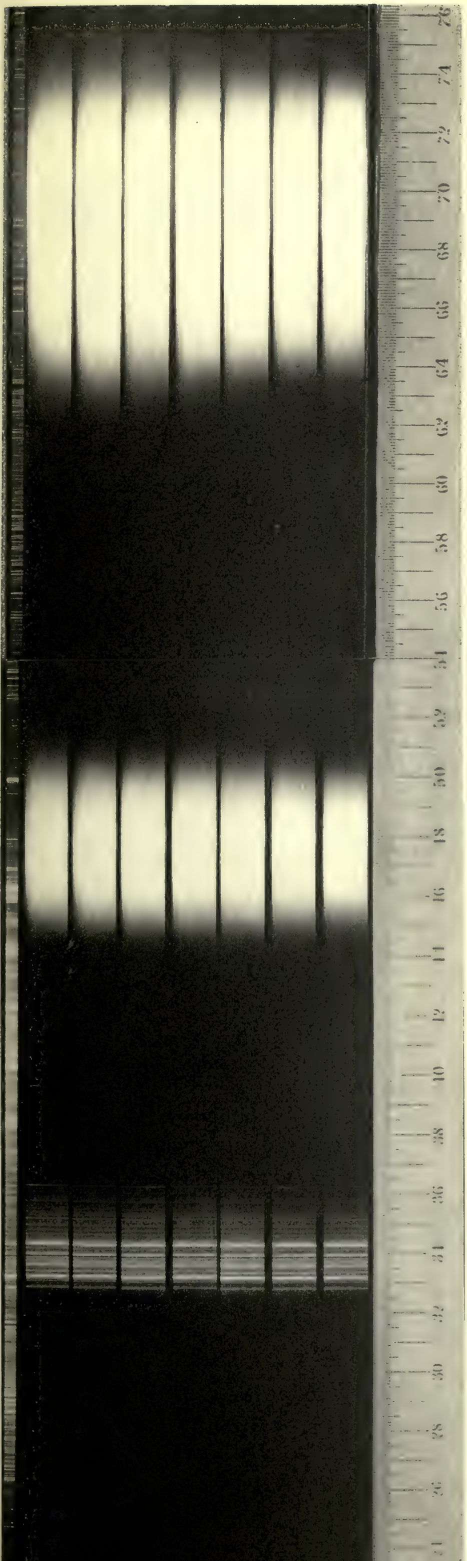

24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

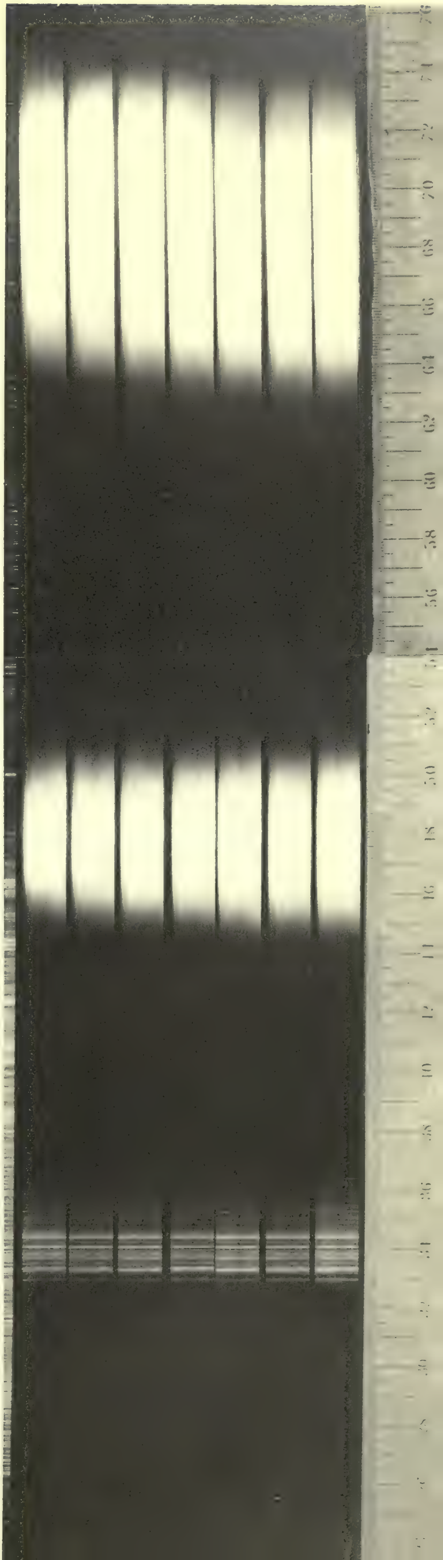

76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

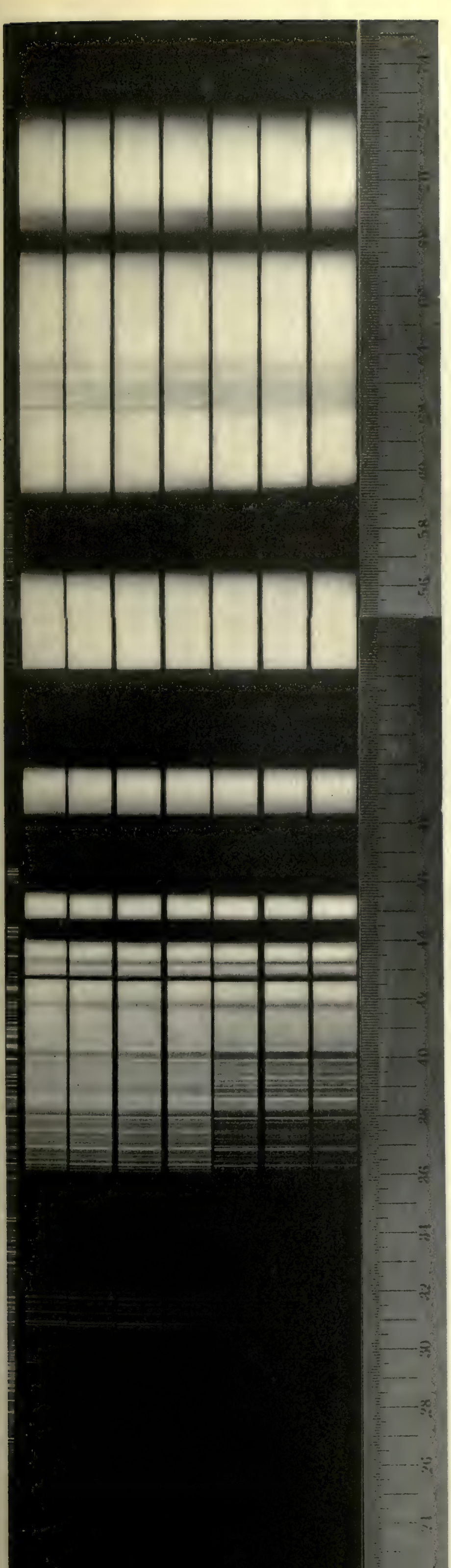
PLAT

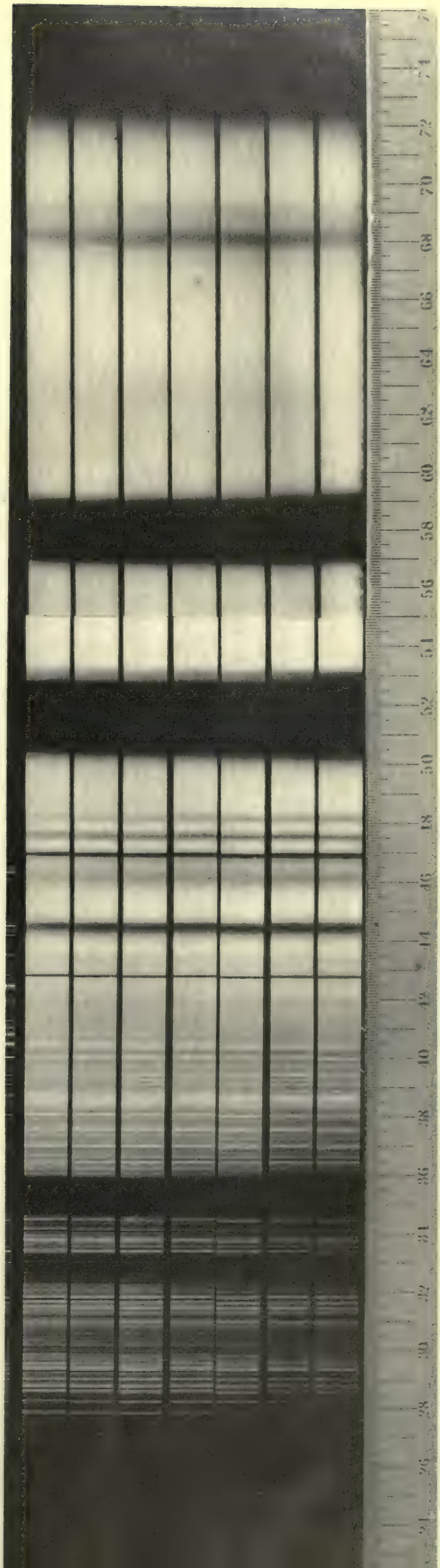

74
72
70
68
66
64
62
60
58
56
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

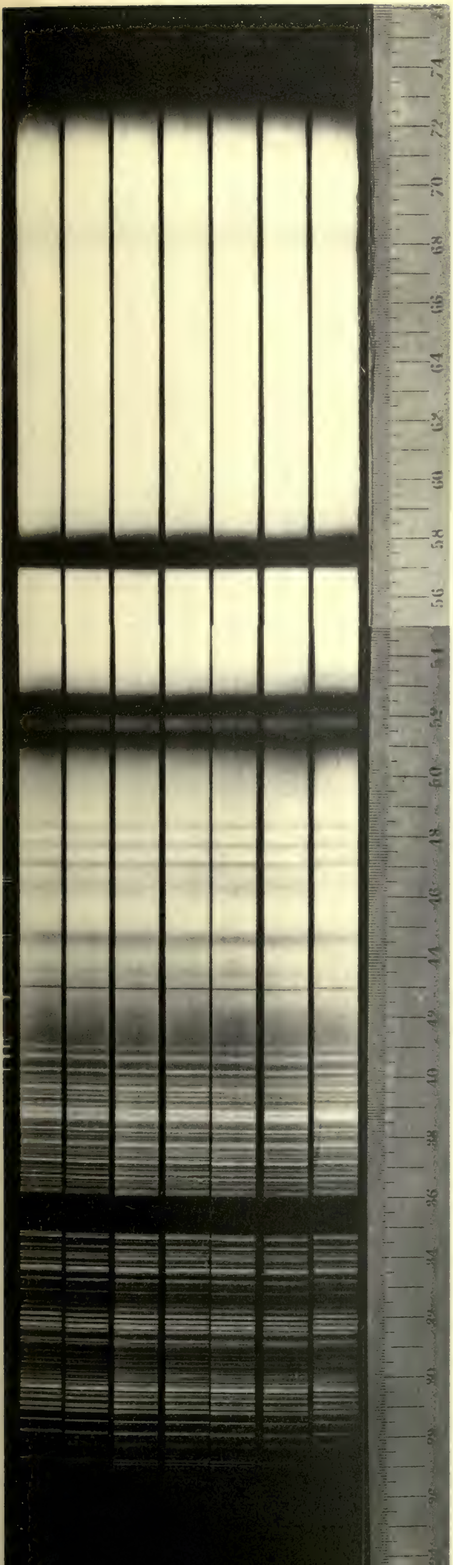


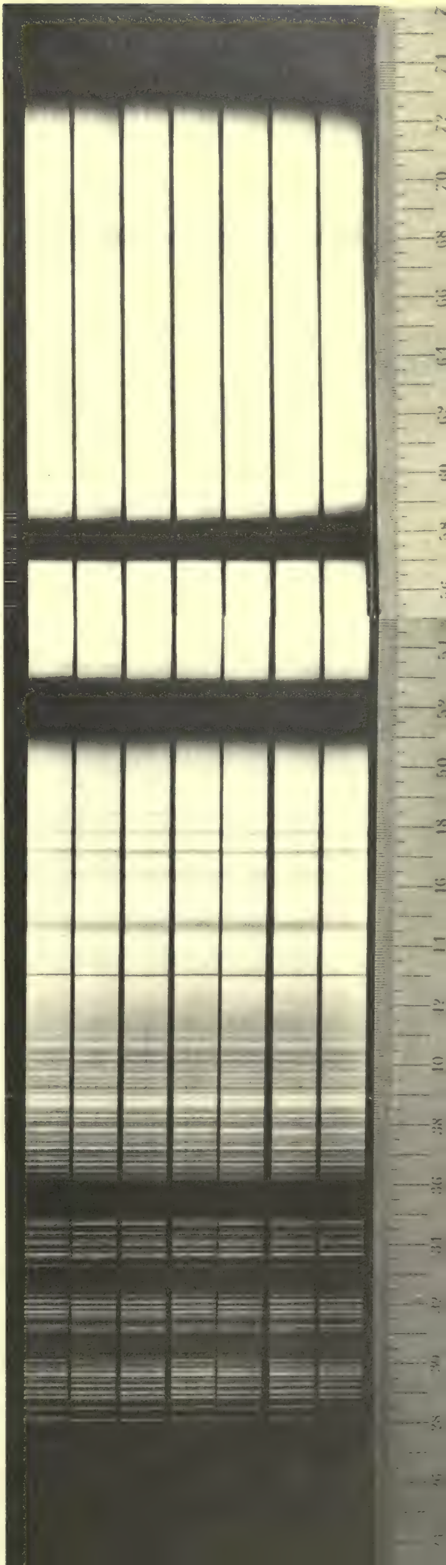

76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

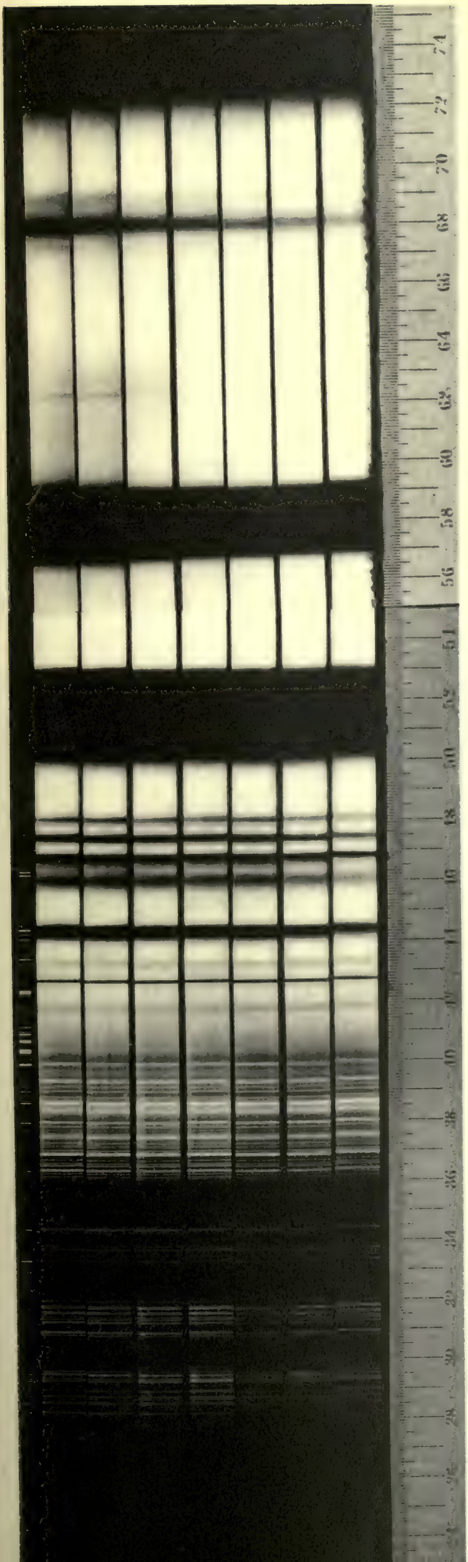

76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

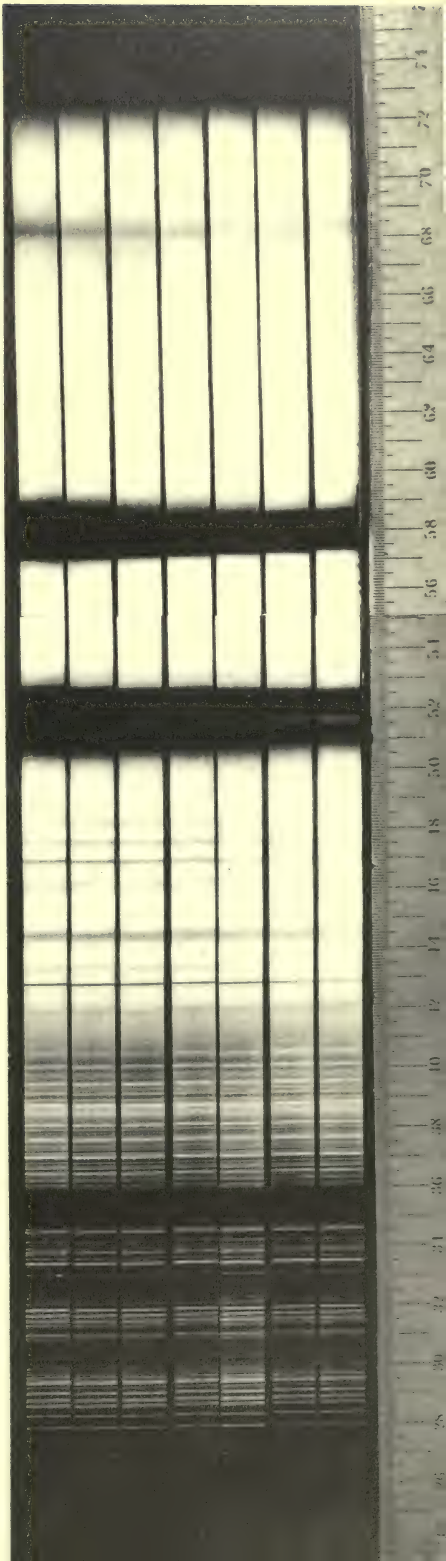

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

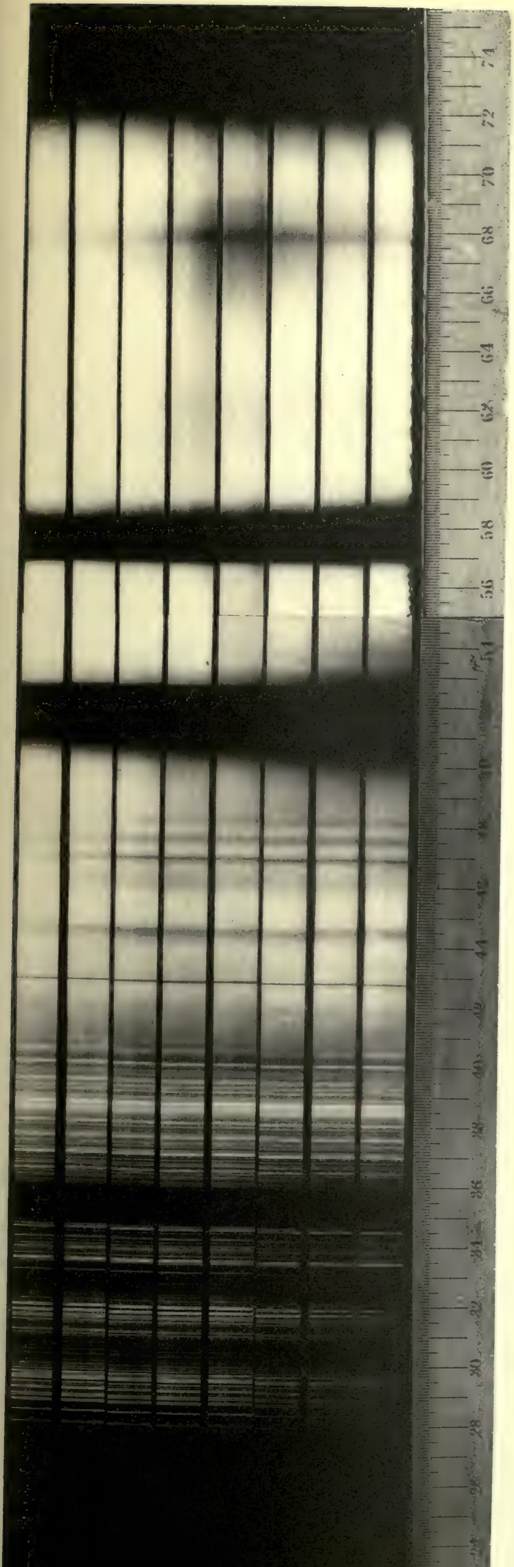

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

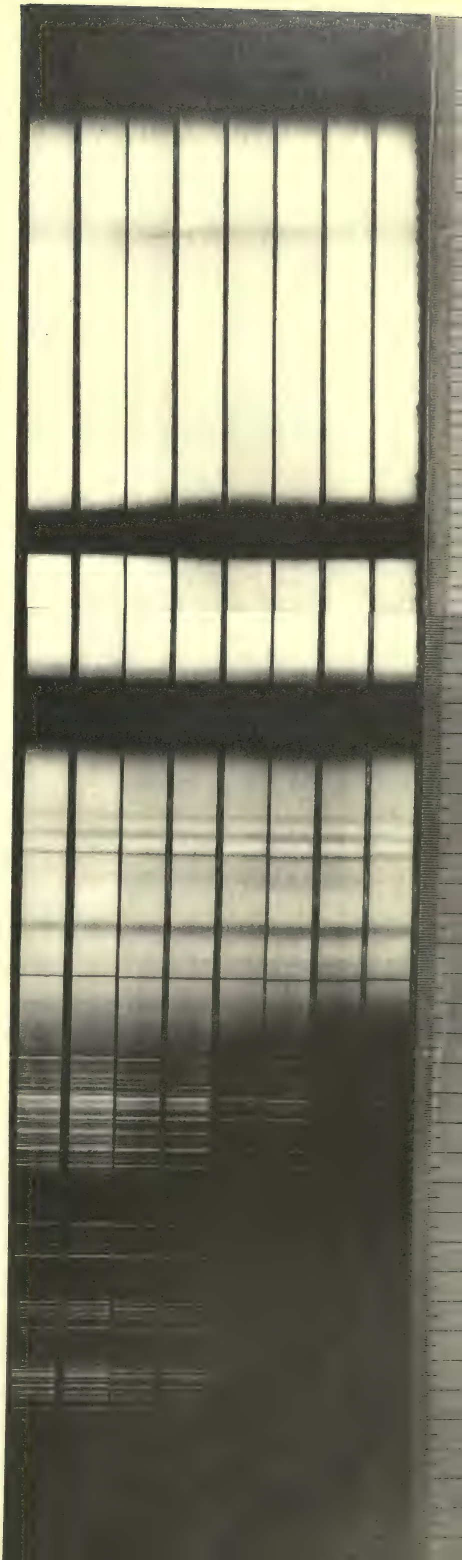

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

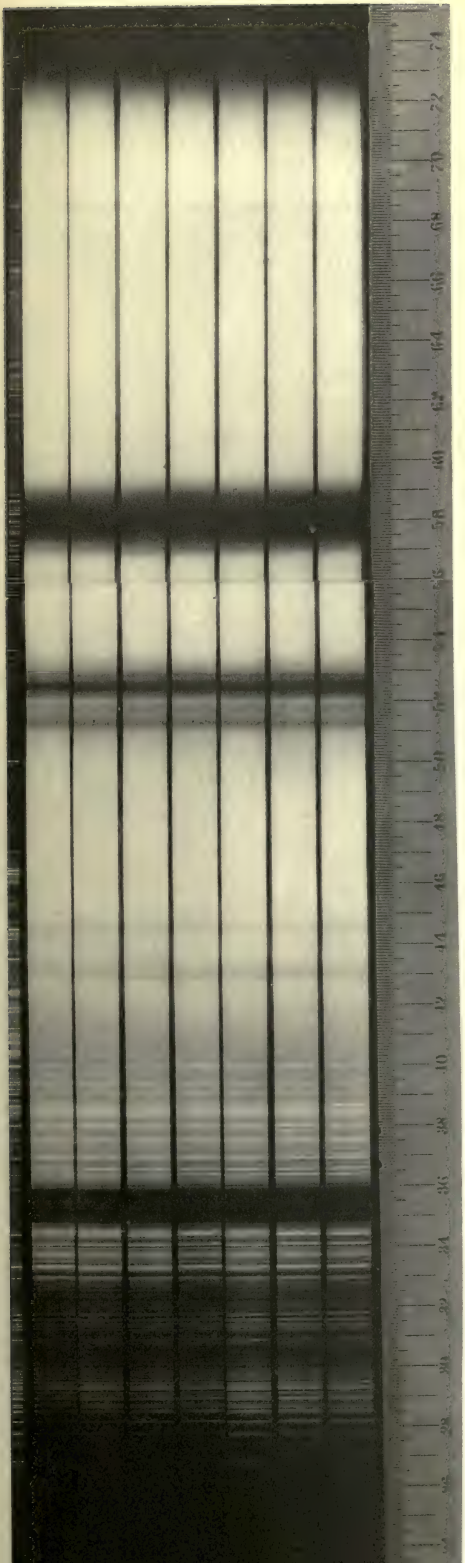

72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28

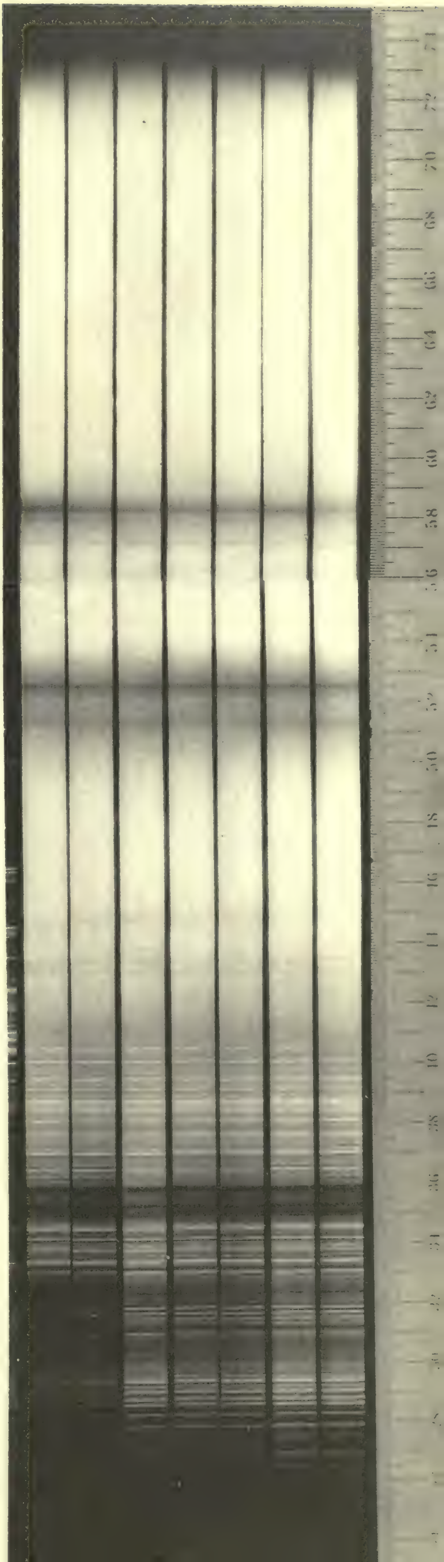

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26

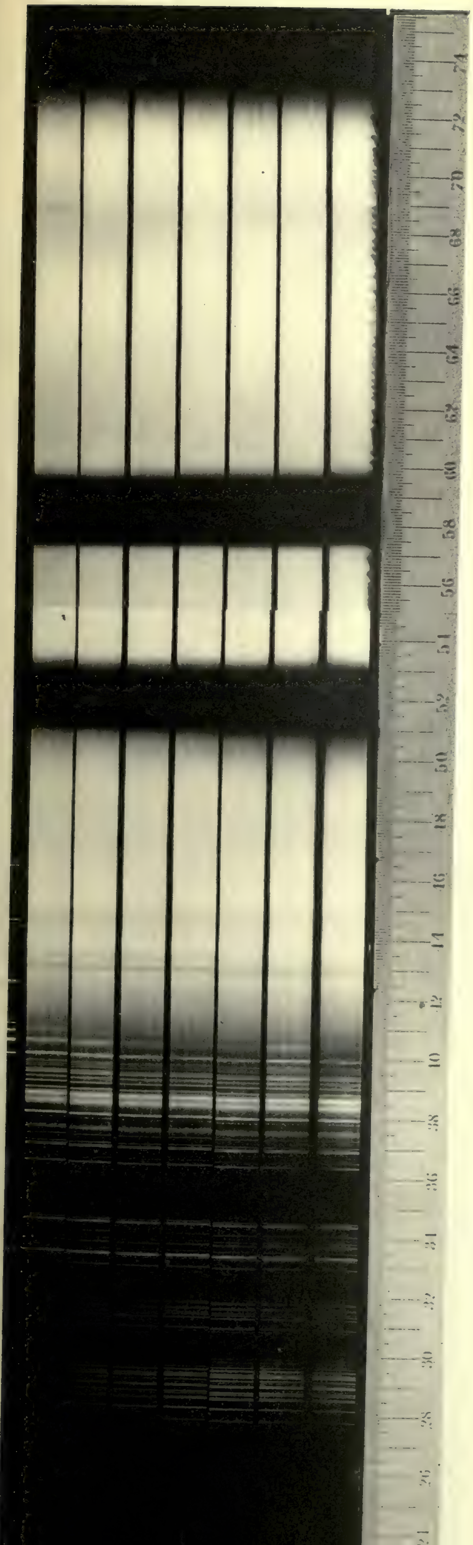

74
72
70
68
66
64
62
60
58
56
54
50
48
46
44
42
40
38
36
34
32
30
28
26

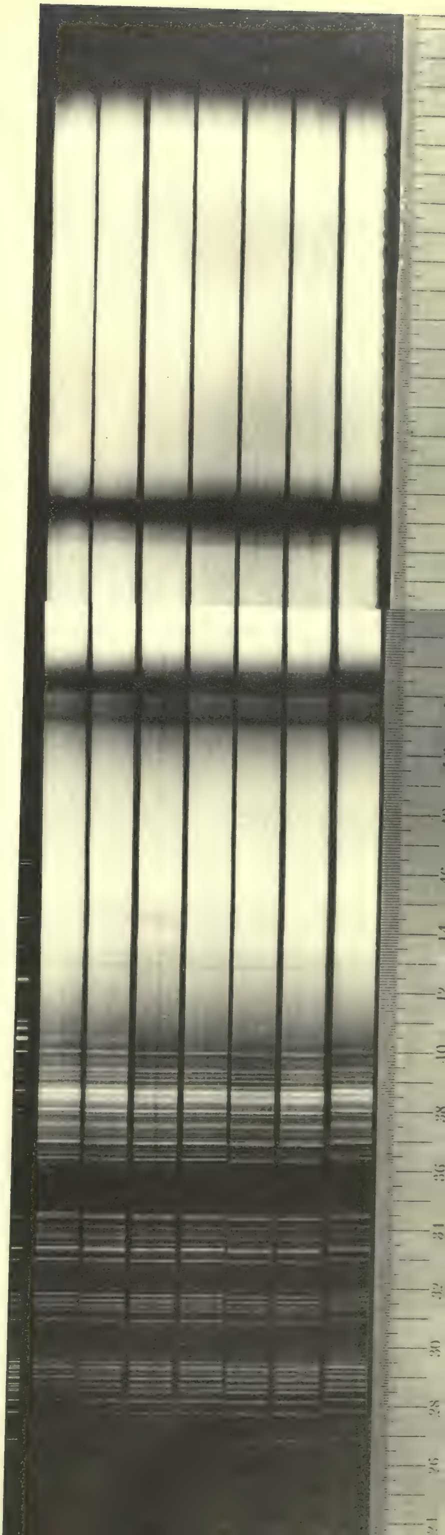


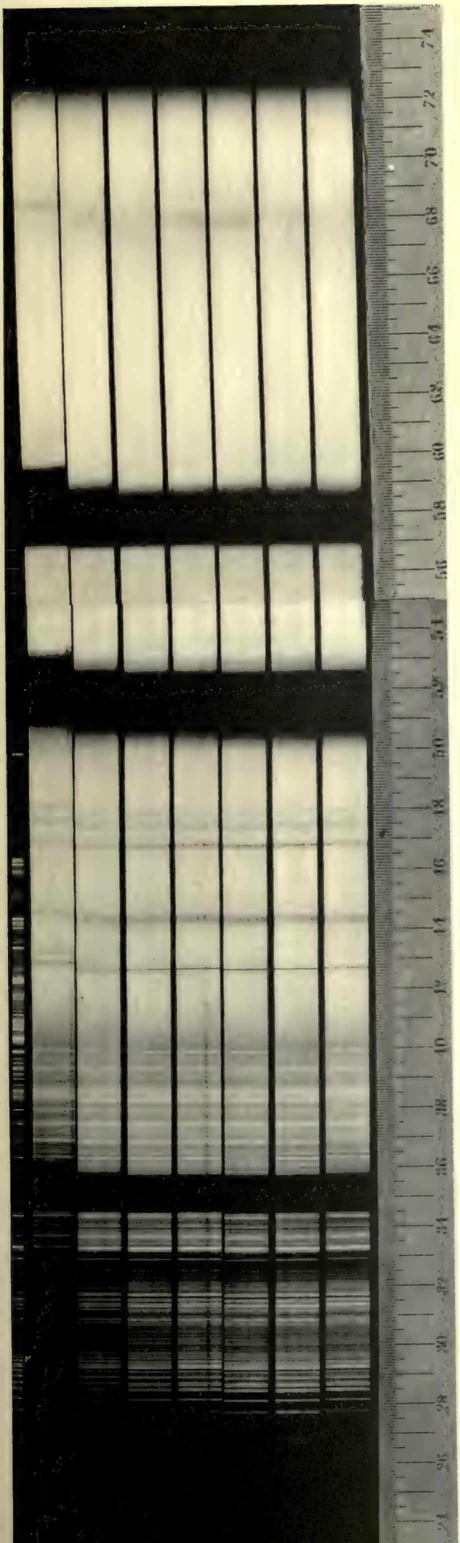

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30

PLA


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24


46
44
42
40
38
36
34
32
30
28
26
24


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

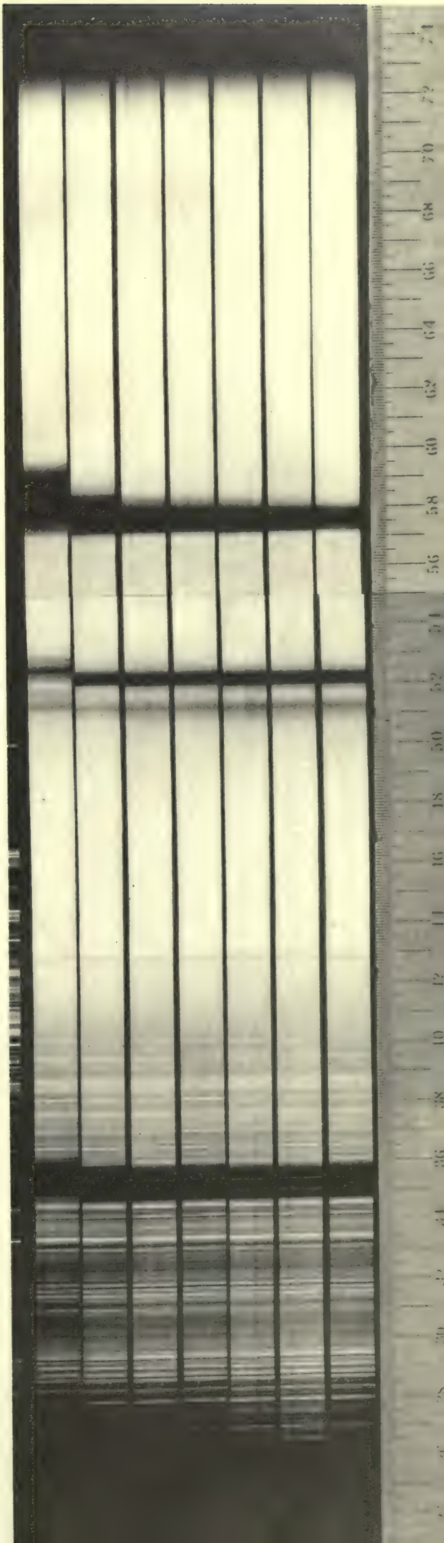
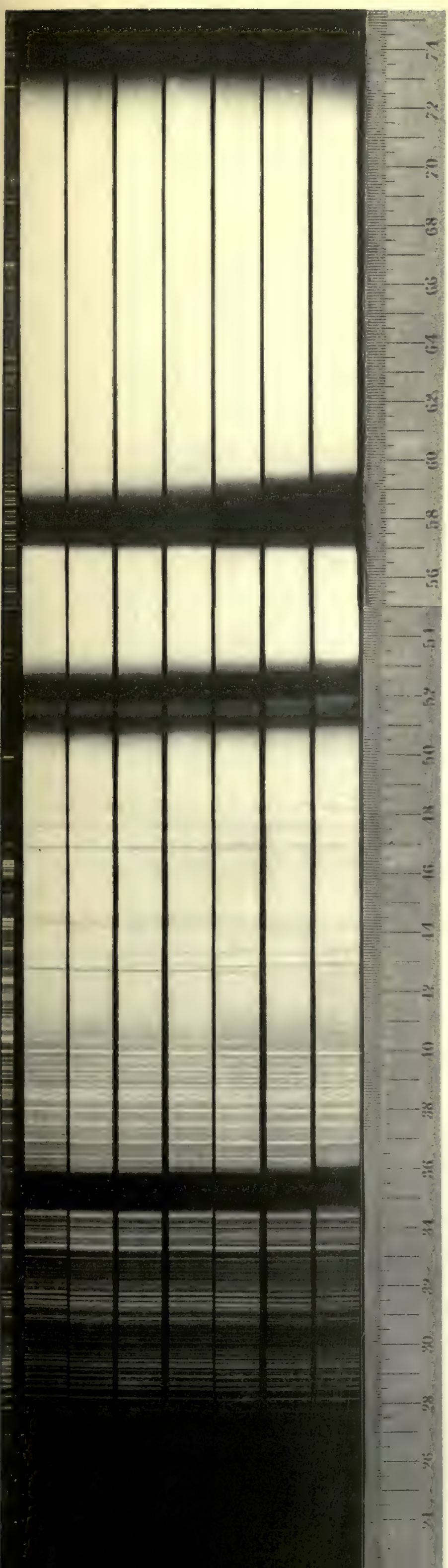
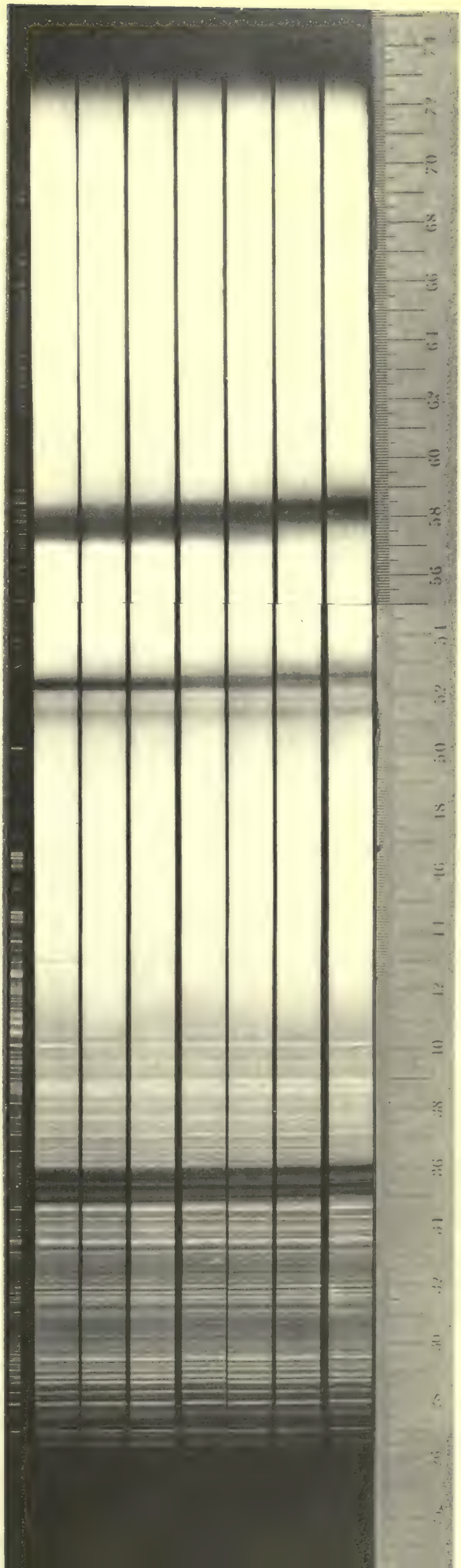
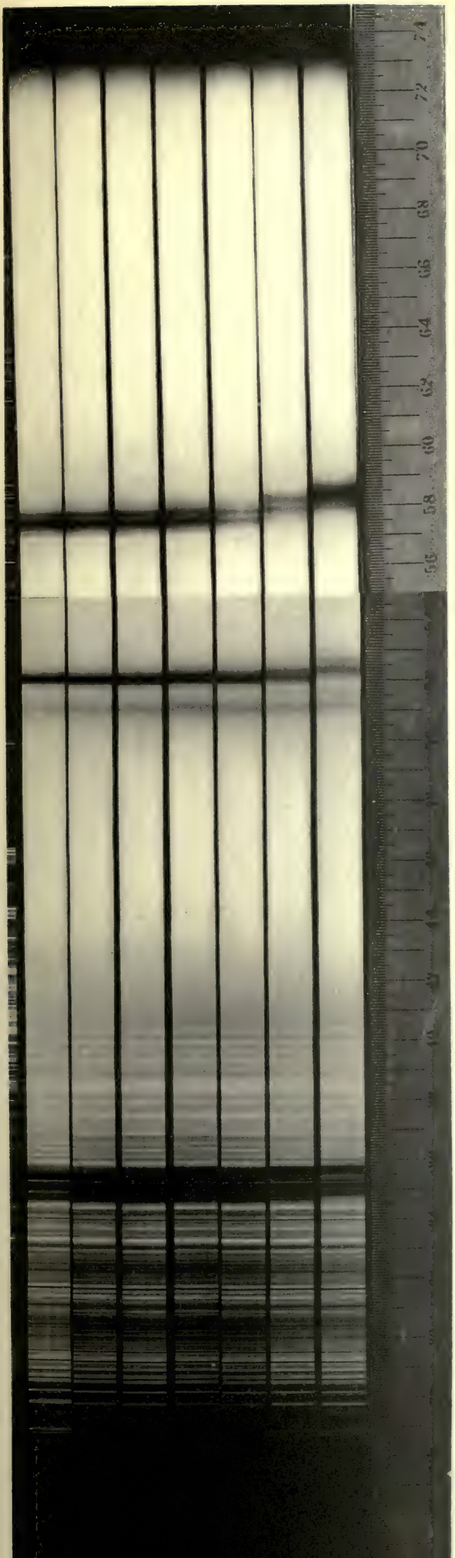
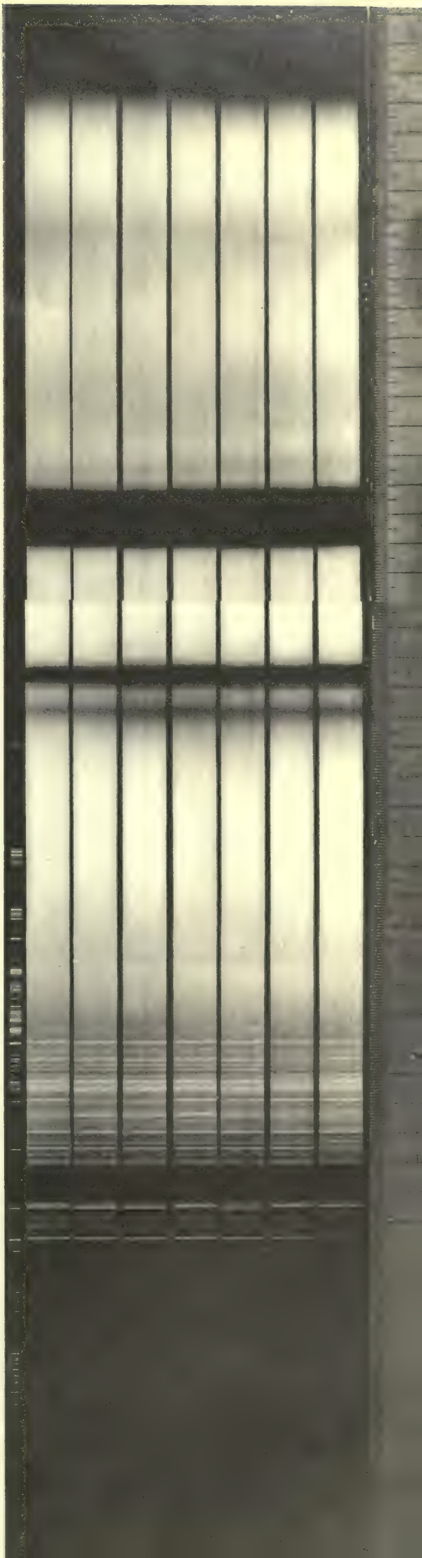

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30

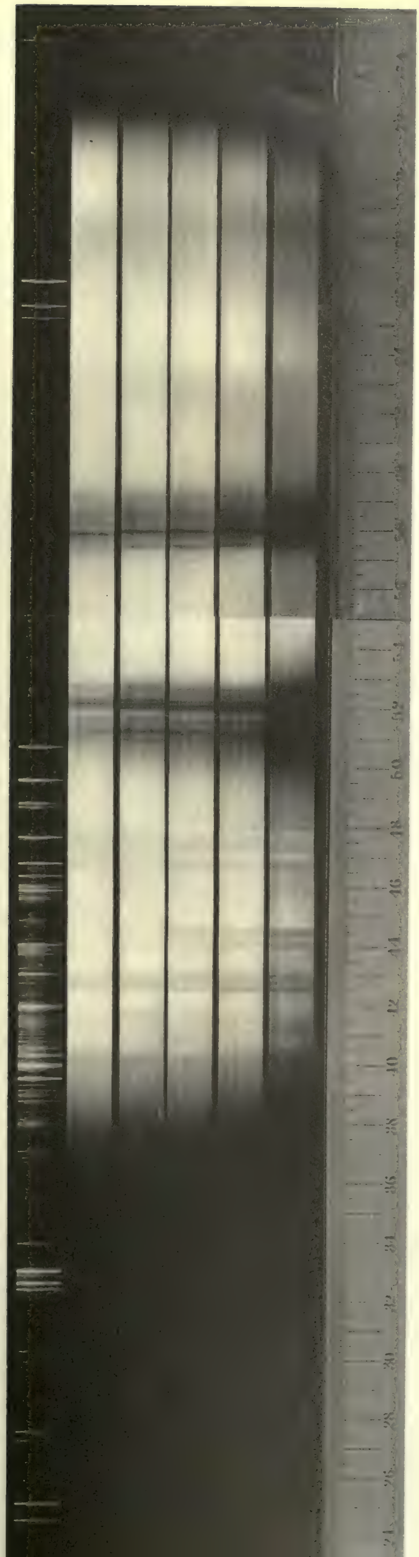
PLATE 66

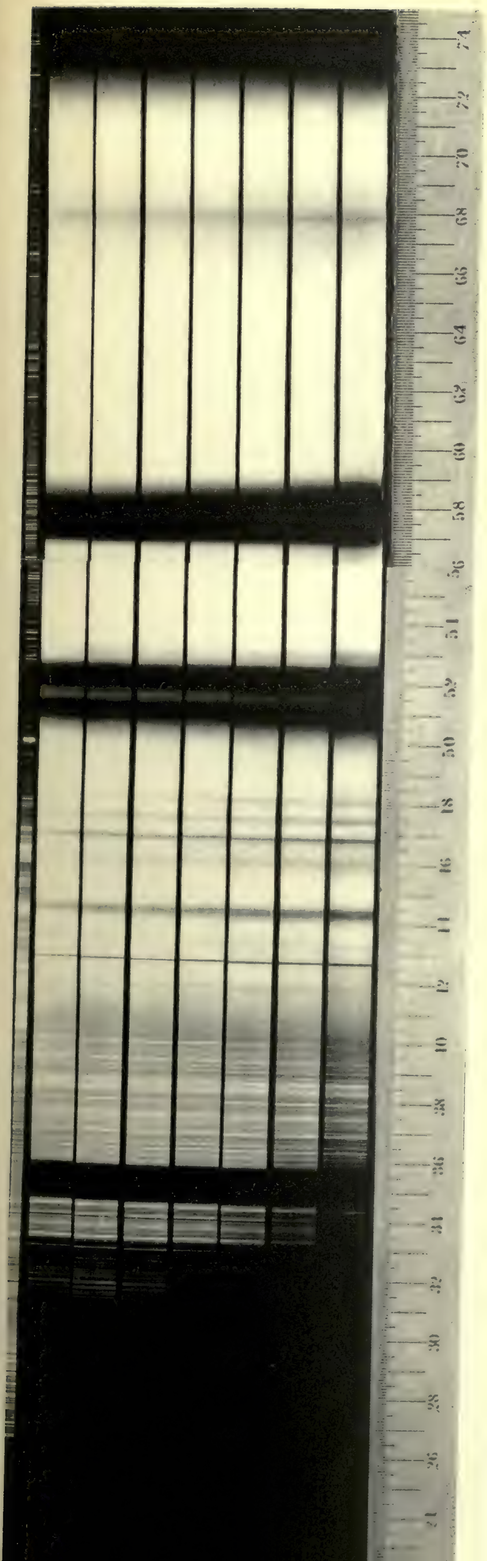

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

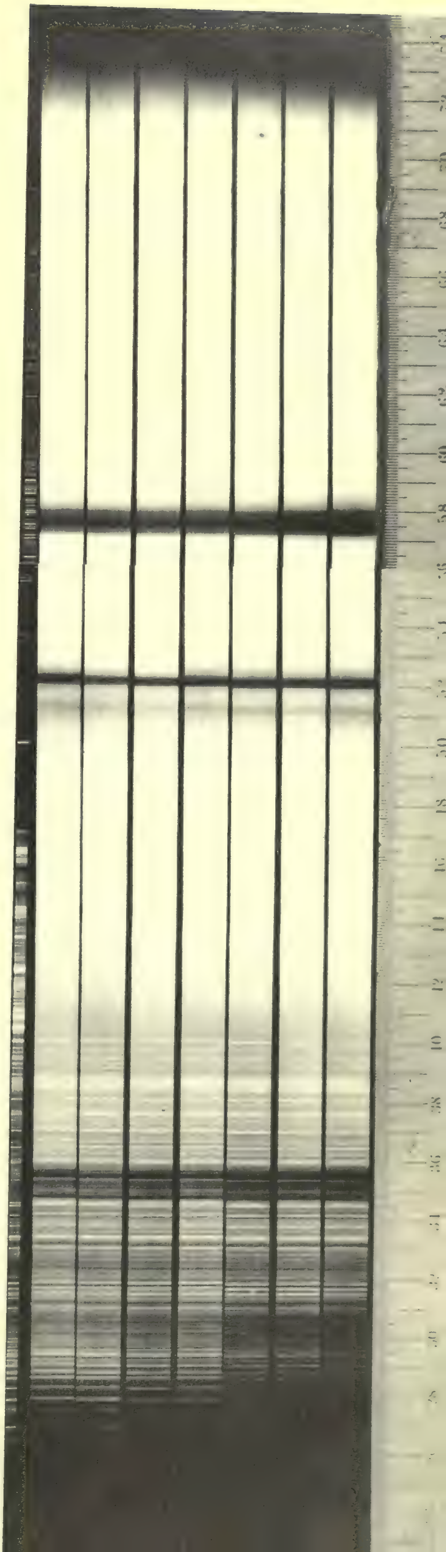

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28


74
72
70
68
66
64
62
60
58
56
44
42
40

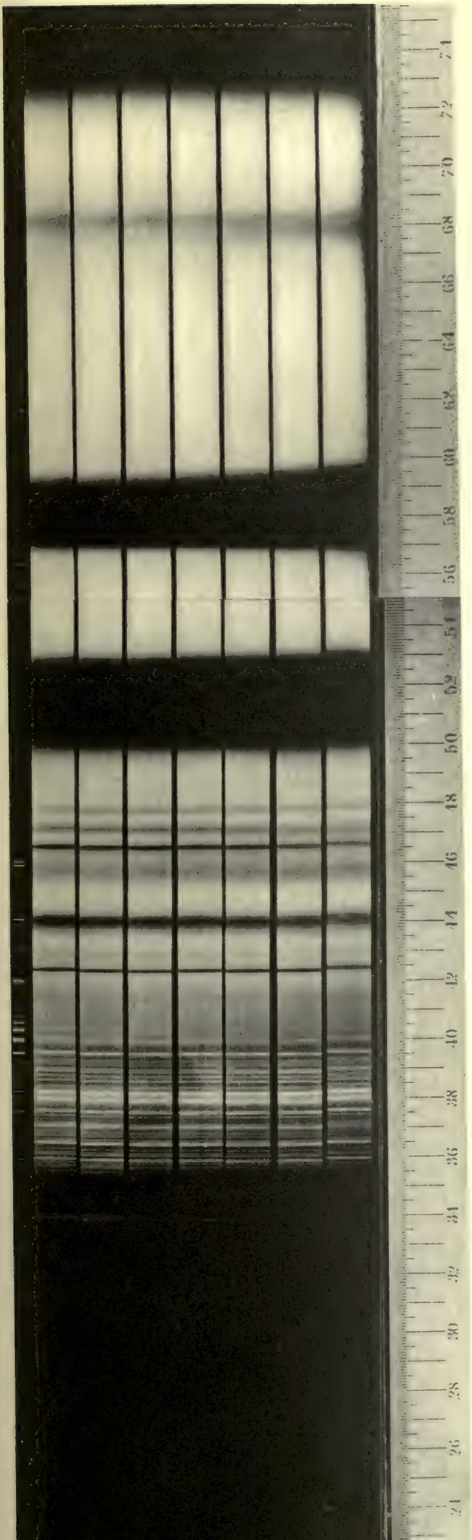



52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

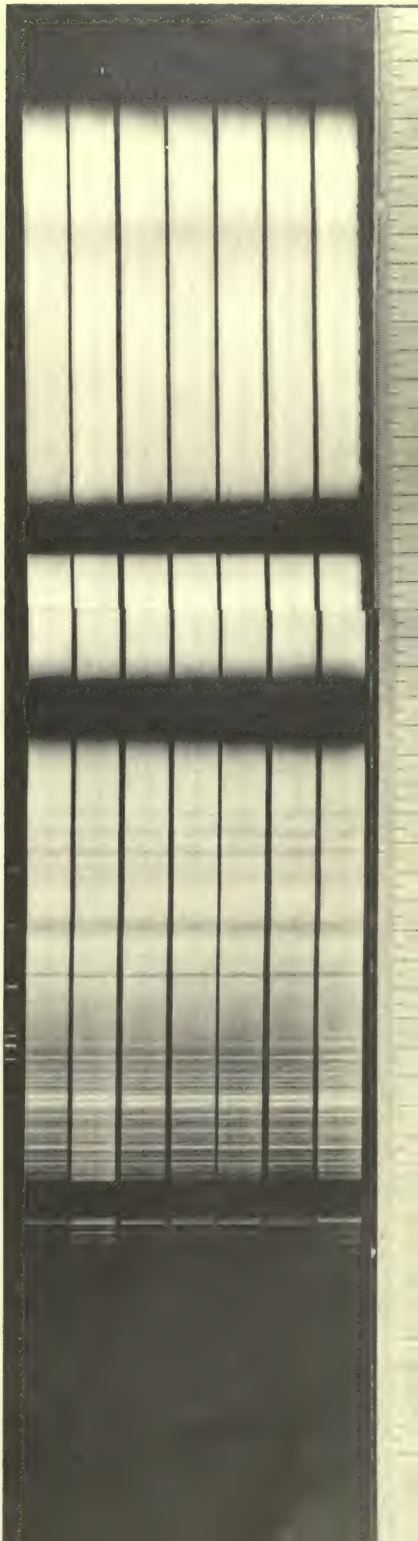

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

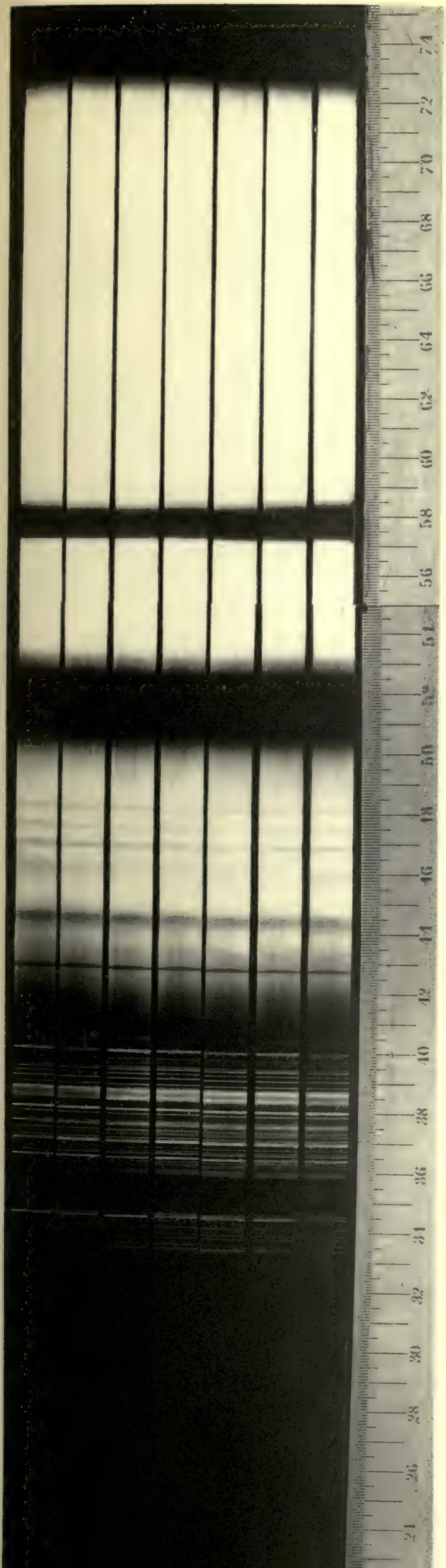


PLATE

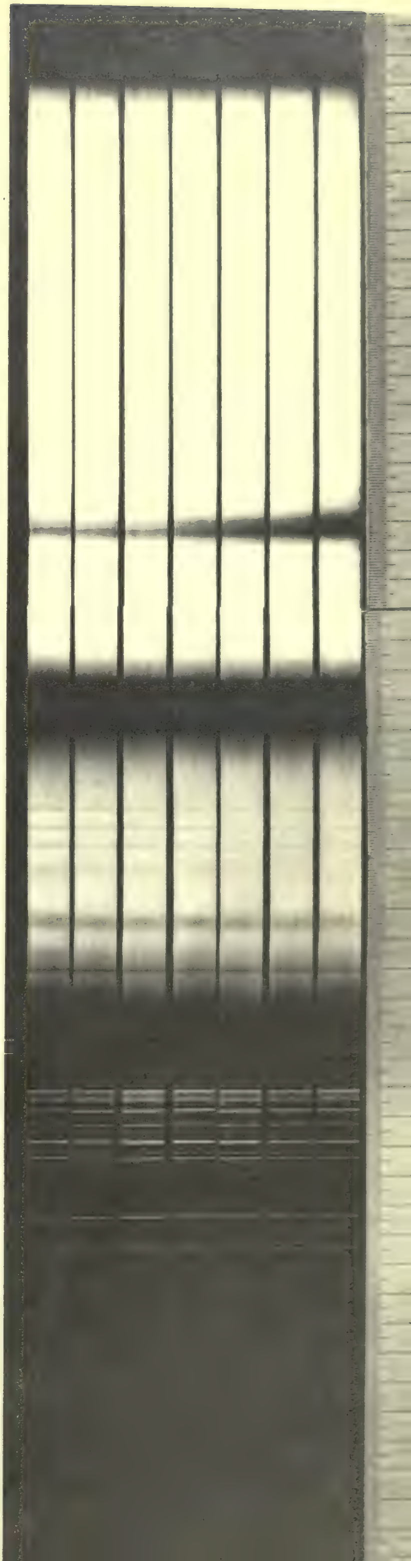


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

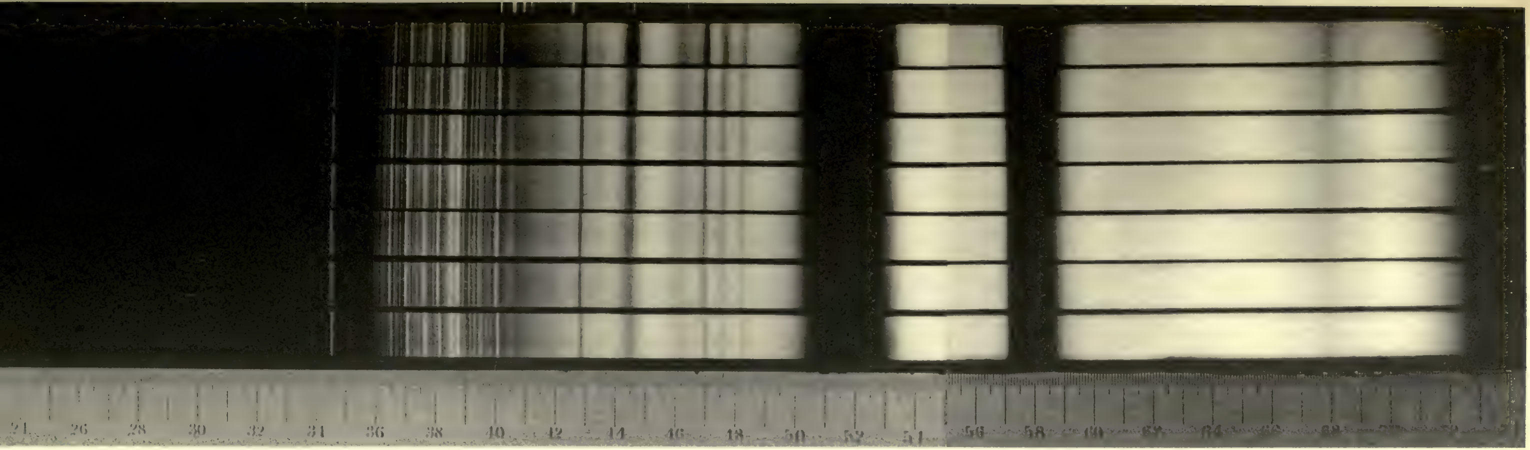




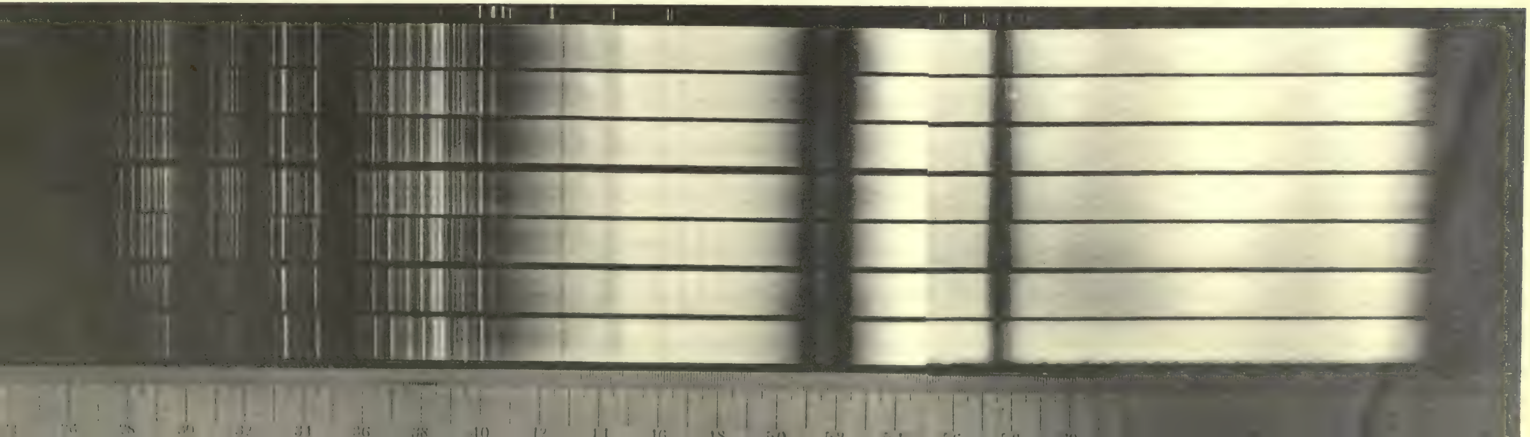
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

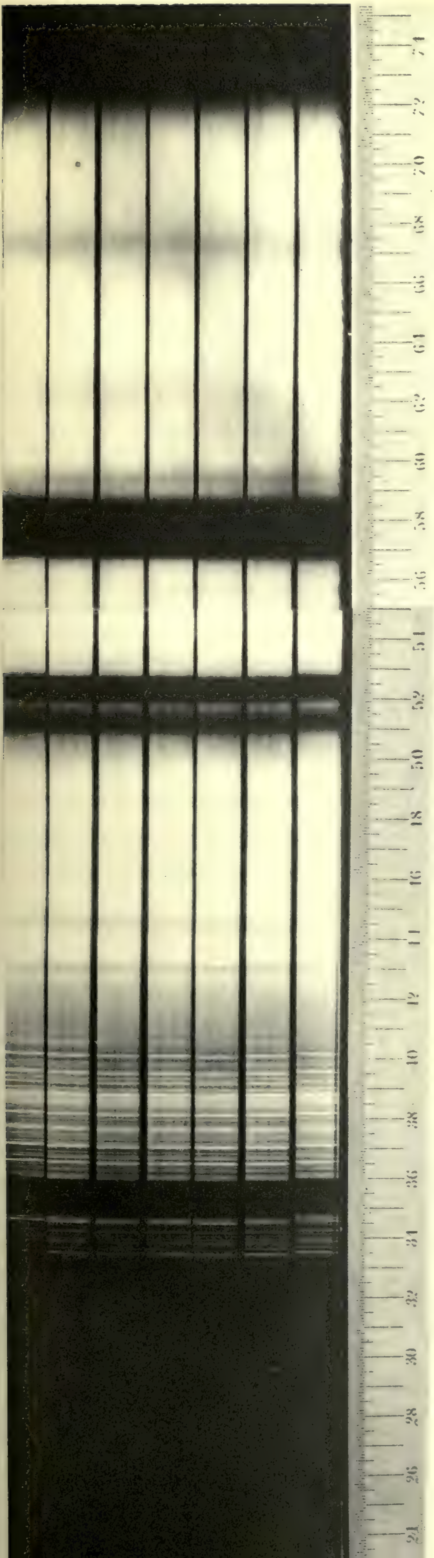


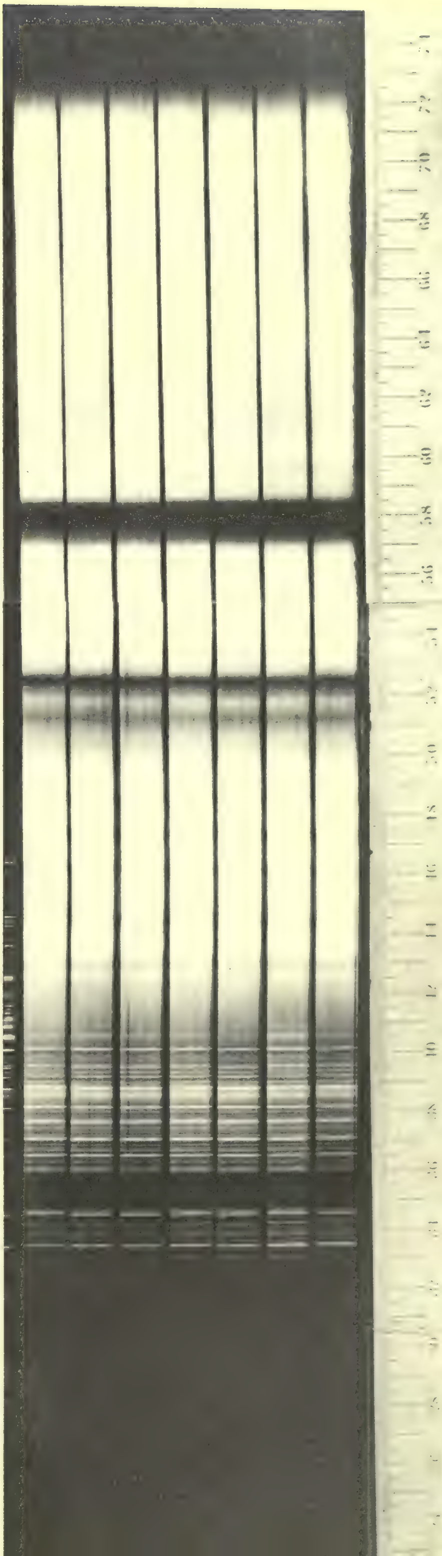
PLATE



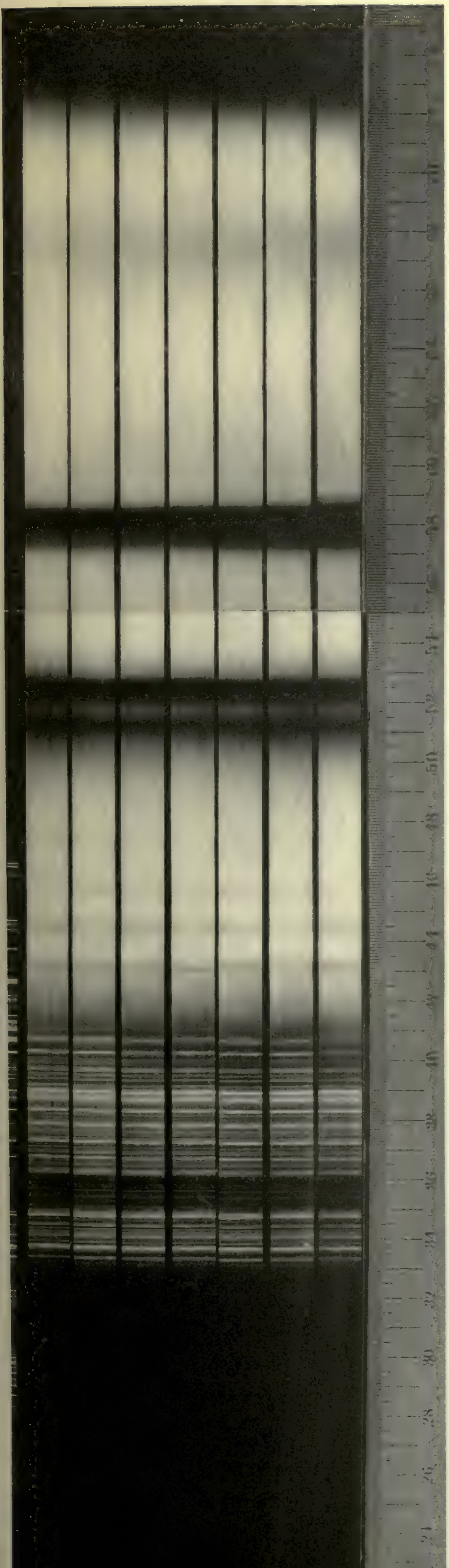
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72



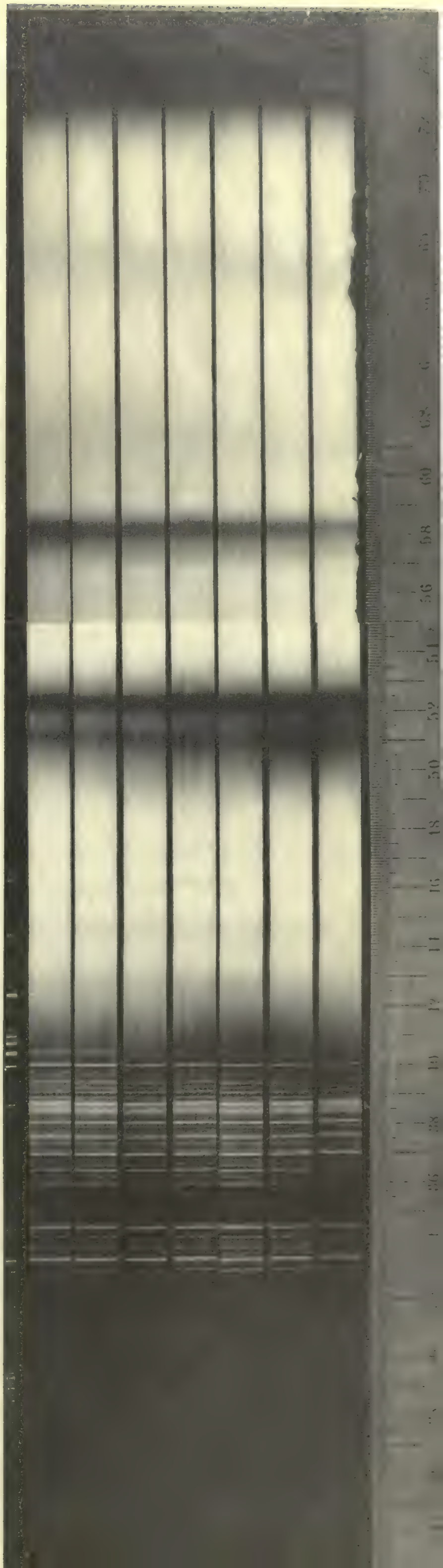

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36

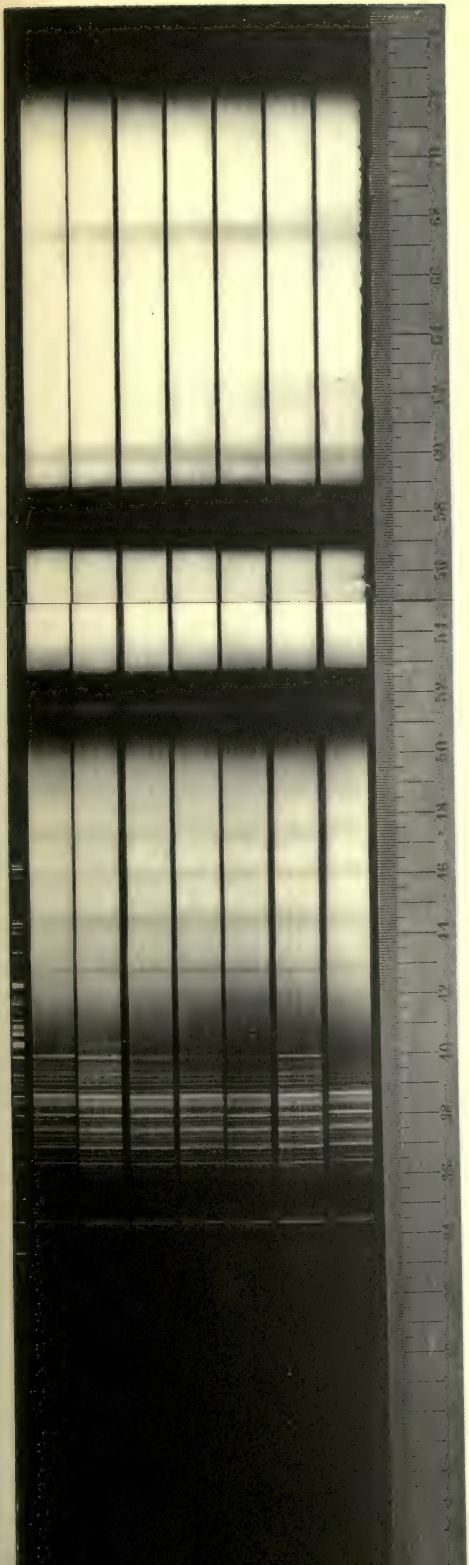
PLATE



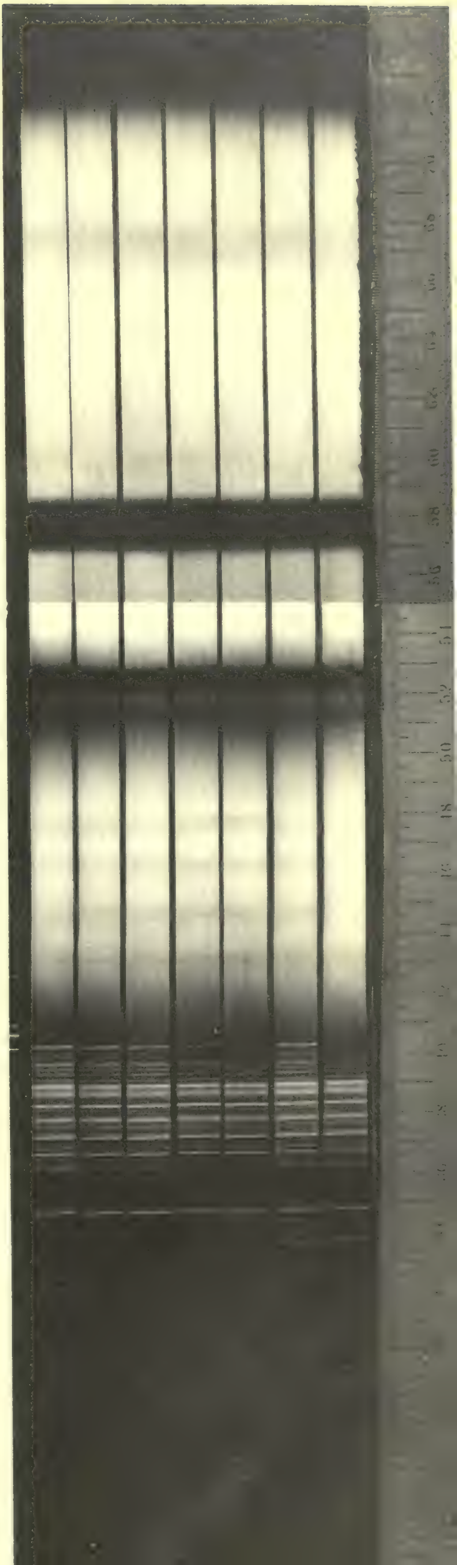
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54



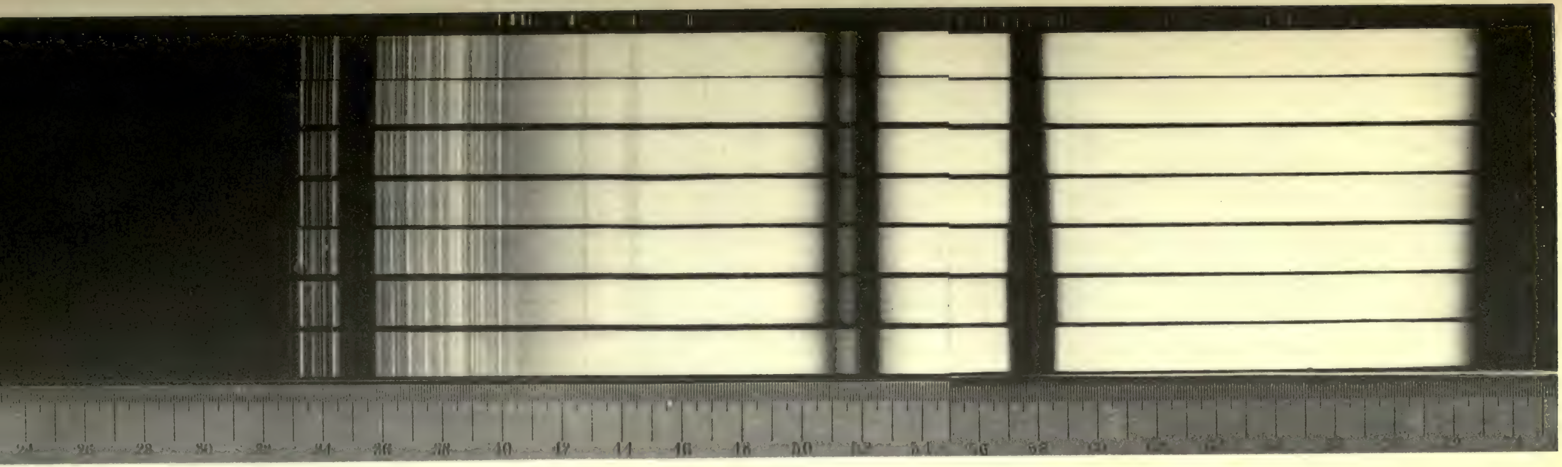
36
38
40
42
44
46
48
50
52
54
56
58
60

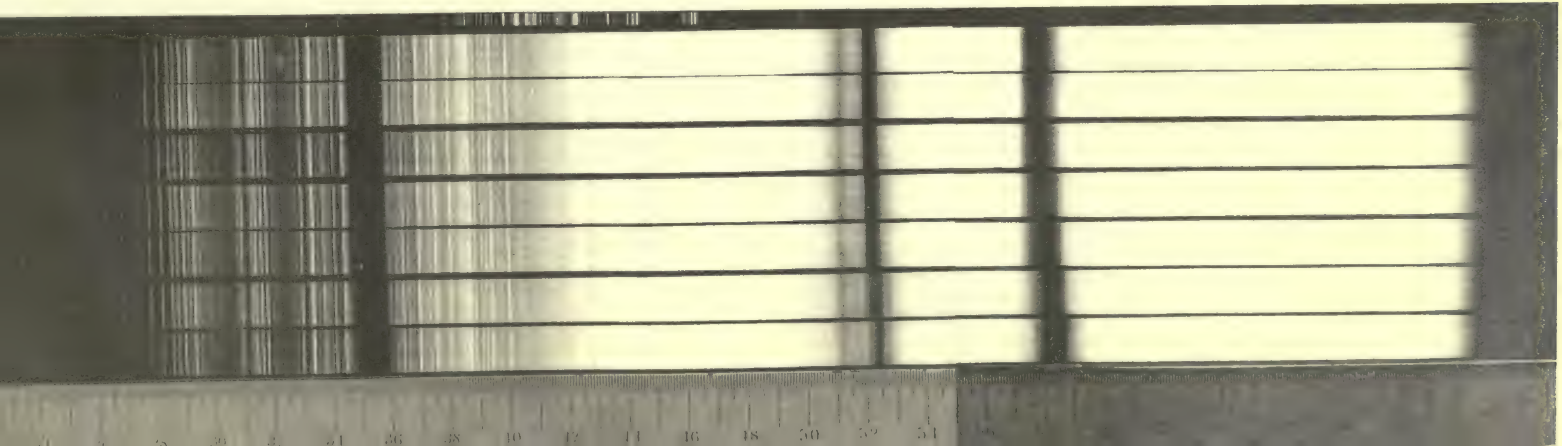


70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34

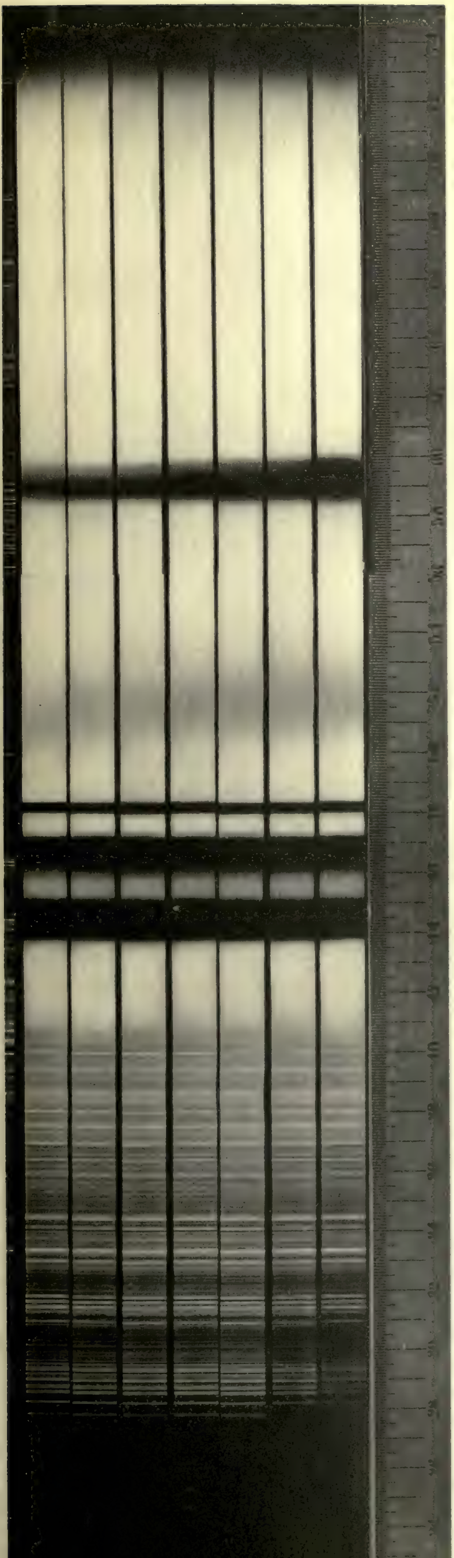


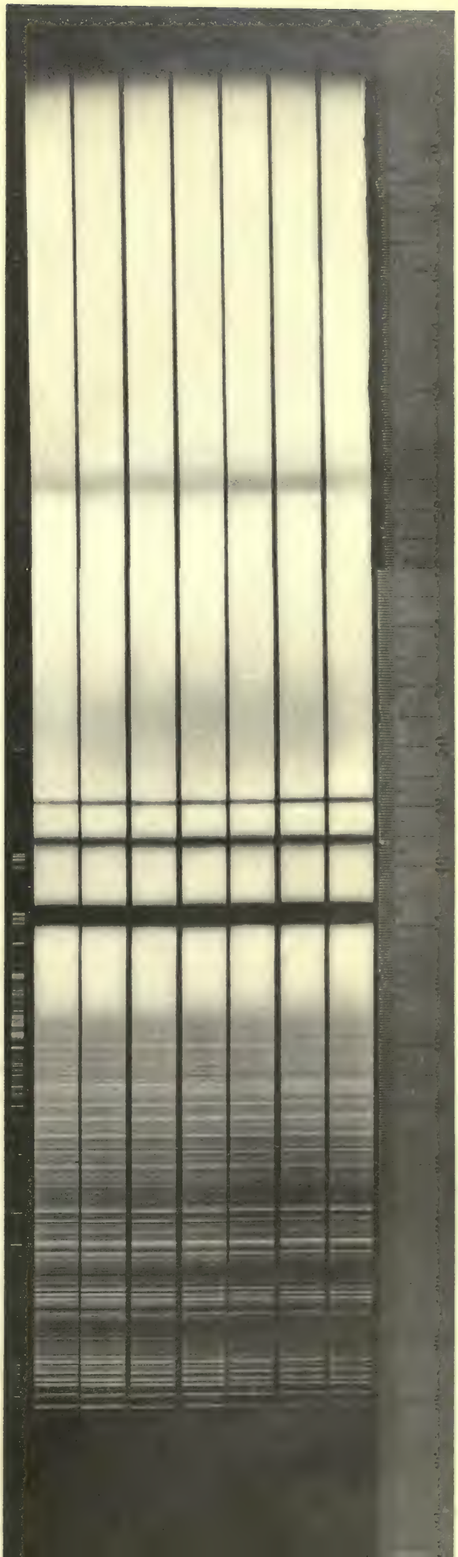
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34

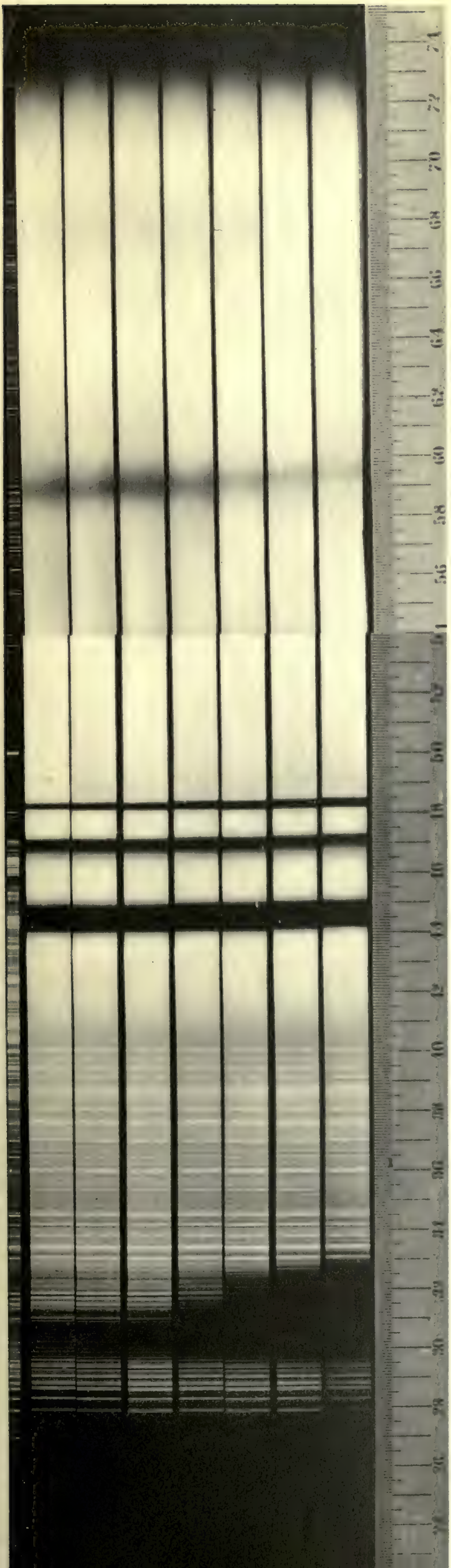

24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58

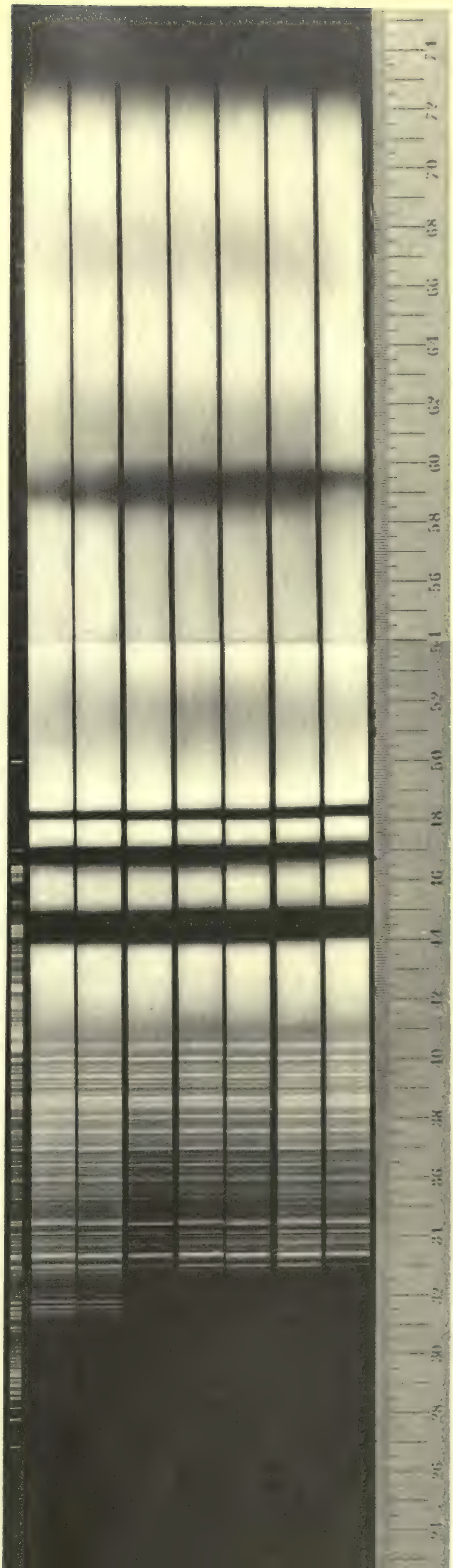

36
38
40
42
44
46
48
50
52
54

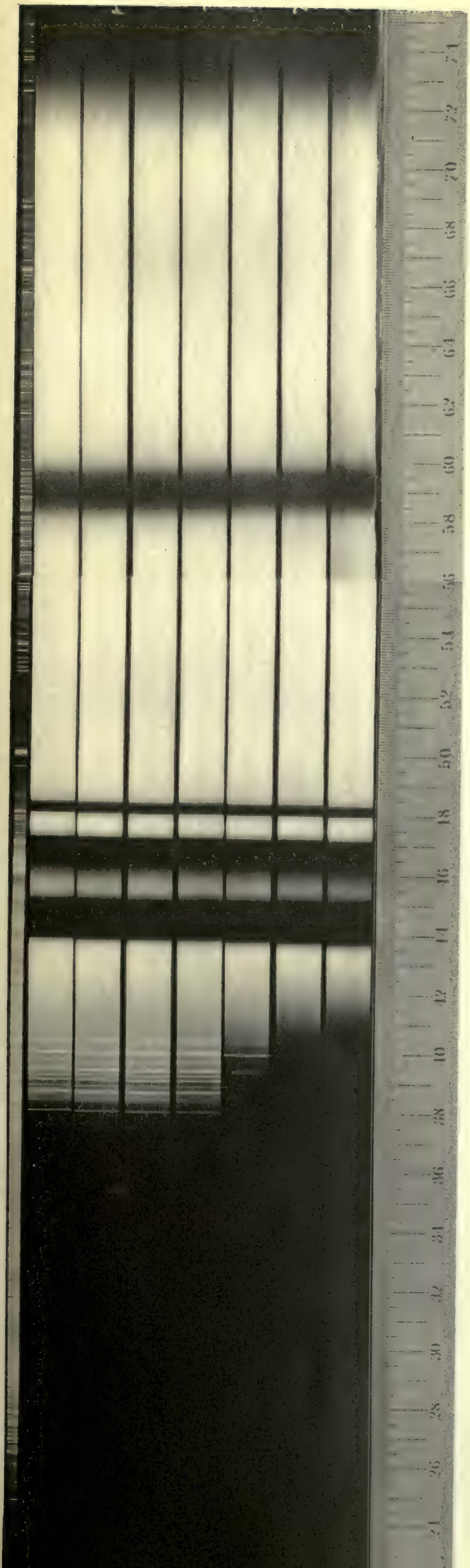
PLATE

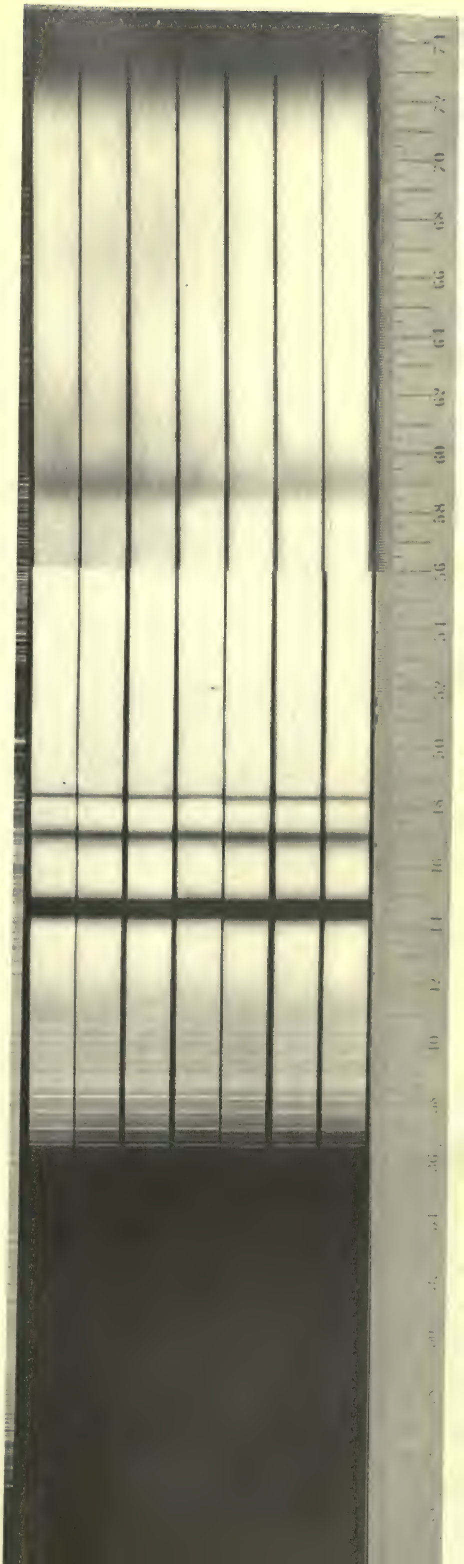




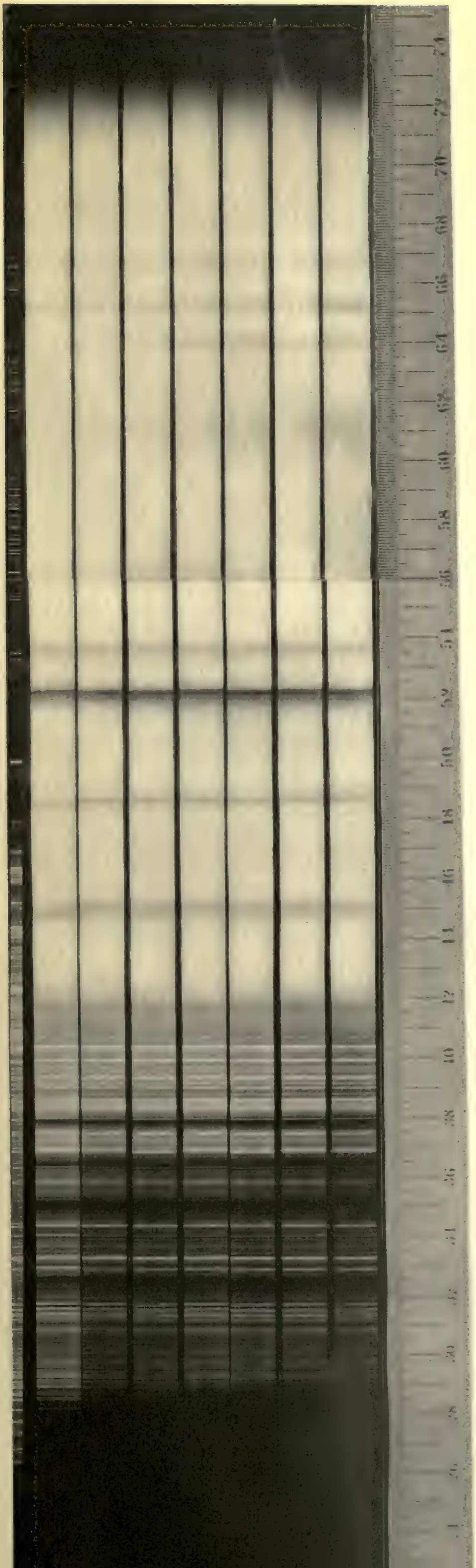

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

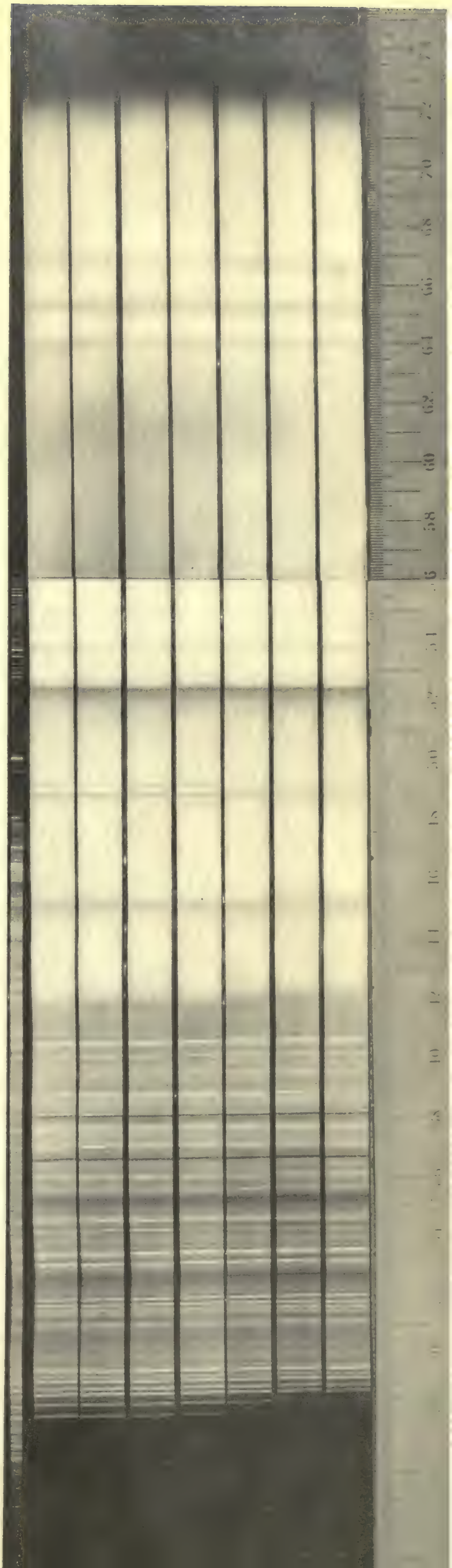

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

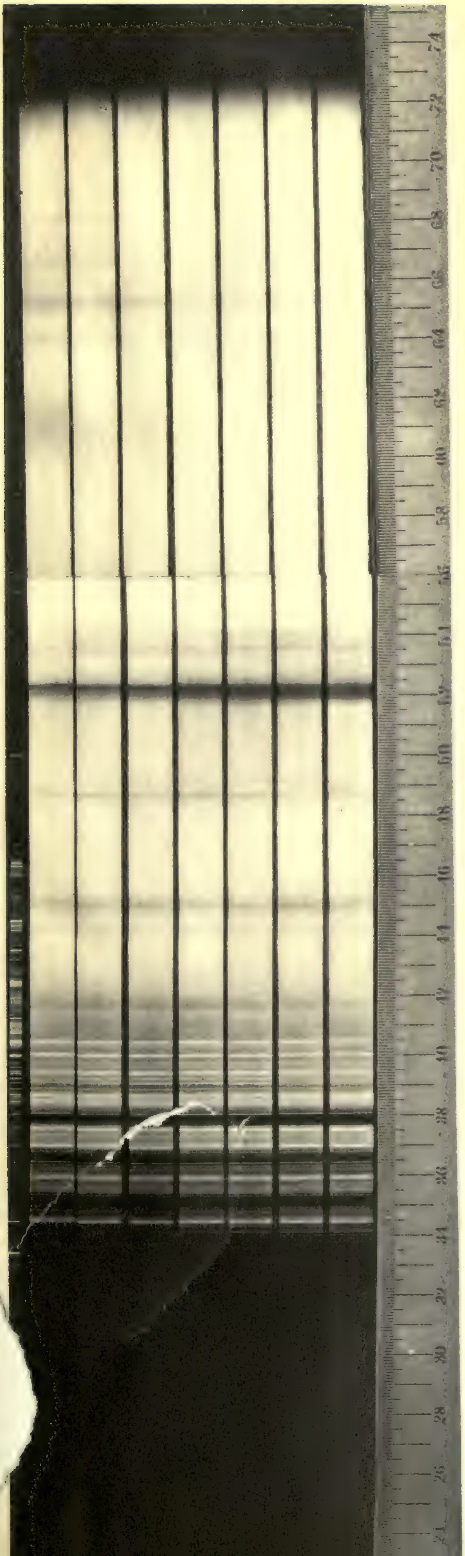

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24

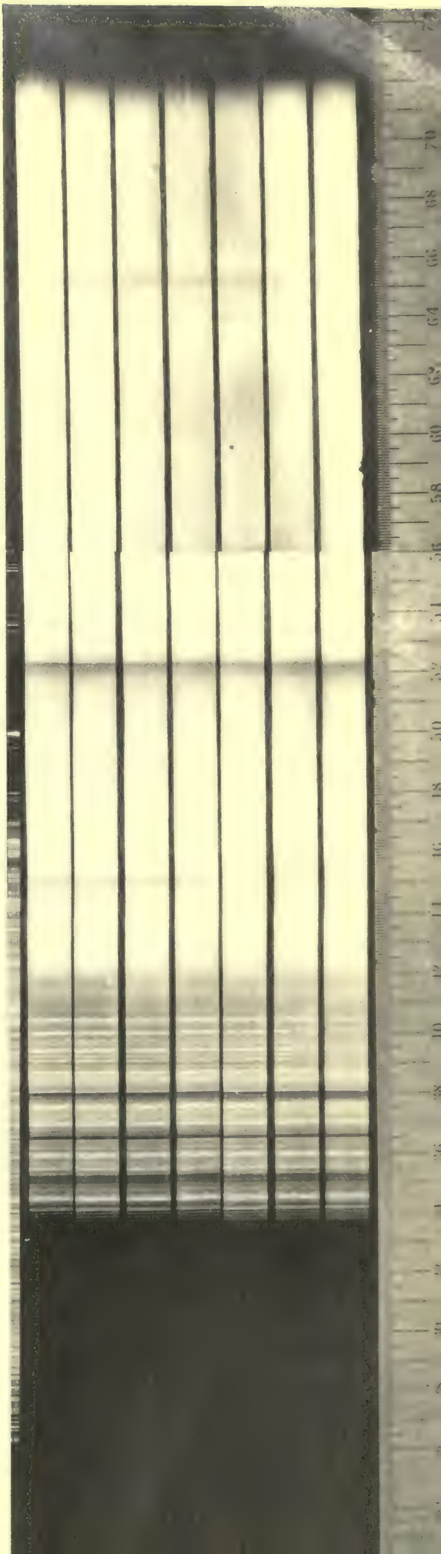

74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34

PLA


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26


74
72
70
68
66
64
62
60
58
54
52
50
46
44
42
40


74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24


70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36

~~617~~
618

PLEASE DO NOT REMOVE
CARDS OR SLIPS FROM THIS POCKET

UNIVERSITY OF TORONTO LIBRARY